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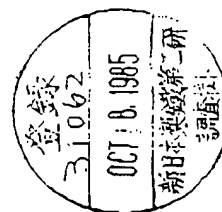
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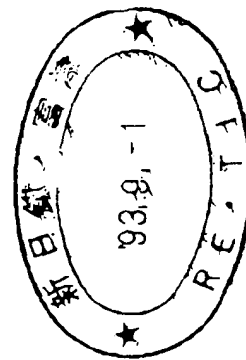
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THE WETTABILITY OF SOLIDS BY LIQUID METALS

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I. INTRODUCTION

Contact between a metal melt and the surface of a solid high-melting substance or material occurs in many physical phenomena and some important technological processes. They include the processes of crystal nucleation and growth from the metal melt, various metallurgical processes-melting, casting, moulding of steel and alloys, soldering and welding, processes of powder metallurgy mineral production by liquid-phase sintering or impregnation of a porous high-melting framework by a liquid-metal binder. Contact systems involving metal melts take place in a number of operating plants where a metallic liquid acts as a working fluid-heat exchanger with liquid-metal heat carriers, nuclear fuel systems where the active substance is distributed as a stable, finely dispersed suspension in the liquid metal, etc.

The contact systems under consideration are usually characterized by developed interphase surfaces, a highly dispersed state of the solid phase, cavities, channels and spaces of small cross-section (capillaries) present in the solid phase. In such systems, as the process advances, the velocity and the direction, as well as the properties of the product obtained, depend on the state and properties of the interface, the degree of wettability of the solid phase by the liquid metal and the contact adhesion strength.

Let us consider several well-known formulae for capillary pressure:

$$p = \frac{k\sigma_{lv} \cdot \cos \theta}{r},$$

for the height of the liquid in the vertical capillary

$$H = \frac{2\sigma_{lv} \cdot \cos \theta}{rg\rho}$$

for the velocity of the movement of the liquid along the horizontal slot

$$L^2 = \frac{\sigma_{lv} \cdot \cos \theta}{6\eta} \tau$$

for the adhesion strength of the liquid and the solid body

$$W_a = \sigma_{lv} \cdot (1 + \cos \theta)$$

where σ_{lv} is the surface tension at the interface of the liquid and gaseous phases, θ the wetting angle of the solid substance wettability by the liquid, r the capillary radius, D the capillary slot width, η the viscosity of the liquid, g the acceleration of the gravity, and τ the time.

Liquid penetration into pores and thin capillary channels of the solid phase and liquid spreading over solid surfaces are elementary processes that determine the state and properties of disperse capillary systems: solid body, liquid, gas (pores).

From the formulas cited above it follows that the progress of these processes is determined by the most important parameters of the system: the wetting angle of the solid body wettability by the liquid (θ) and the surface tension of the latter (σ_{lv}).

Bottom boiling (nucleation of carbon monoxide bubbles and steel decarbonization in the open-hearth bath, growth and removal of non-metallic products of deoxidation) depend respectively on the degree of wettability of the furnace bottom and the non-metallic inclusion of the liquid metal.

With a high degree of wettability (strong adhesion and the liquid to the solid surface), nucleation of bubbles at the interface steel-bottom is hampered or stops at all well wetted non-metallic inclusions with strong adhesion to the metal. The bubbles hardly coalesce and are not removed from the steel bath.

At a low degree of wettability of the solid body by the liquid metal ($\theta > 90^\circ$) it is impossible to realize the process of liquid phase sintering or impregnation of mineral bodies. Here liquid metal displacement from the solid framework pores is taking place. This is known in sintering technology as "sweating."

The degree of wettability and adhesion of the metallic binder

to the high-melting component of cermet determines many properties of the material obtained: the degree of phases dispersion, character and uniformity of their distribution, the material strength, its physical and other characteristics.

While using the liquid metal as a heat carrier, film boiling occurs in the case of poor wetting of heat exchanger walls which sharply lowers heat removal. The solder badly wetting the surfaces being soldered does not penetrate into the gap between the parts to be connected and cannot form a strong bond between them. The process of soldering proves to be impossible.

Measuring the degree of wettability of solid bodies surfaces by liquid metals makes it possible to determine the energetic parameter of interaction between the pair of substances, i.e., the work of adhesion. For systems with a rather low degree of interaction (solid bodies insoluble in the liquid metal and nonwettable by it) it is practically impossible to obtain such characteristics by any other method (calorimetric, for instance). The method of measuring wettability for such purposes becomes the only one.

One can measure the degree of wettability, which depends on the liquid and the solid phase composition, and construct a composition-property diagram using the method of wettability by the liquid as the means of physico-chemical analysis.

Thus the study of contact and capillary properties of metal melts, the processes of wetting solid bodies surfaces by them, and metal adhesion to the solid surface constitutes one of the most important aspects of modern metallurgy, physics and physical chemistry of solid substances and metallic liquids.

The phenomena of wettability and adhesion have been studied during the 14th through the beginning of the 20th century in low-temperature contact systems formed by various solid bodies and organic liquids, water, mercury, among others. Solid body wettability by molten metals at high temperatures under the conditions of chemical interphasic reactions possesses a number of

independent problem.

The present paper deals with the problems of physico-chemical wetting, contact and capillary phenomena in metal melts at high temperatures.

II. GENERAL LAWS OF THE WETTING OF SOLIDS BY LIQUIDS.

WETTABILITY BY LIQUID METALS

The main thermodynamic relations of the wetting theory are the equations for wetting angle (θ) and the adhesion work (w_a):

$$\cos \theta = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} \quad (1)$$

$$w_a = \sigma_{lv} \cdot (1 + \cos \theta) \quad (2)$$

where σ_{sv} , σ_{sl} , σ_{lv} are interphasic specific surface energies at the interfaces solid body-gas, solid body-liquid and liquid-gas (Fig. 1).

Both of the above equations were proposed in 1804 by T. Young [1] without strict proof. These equations were then obtained theoretically by different methods [2-9] ranging from the mechanical equilibration of forces at the three-phase boundary to the use of variational methods [2,8,11] or from thermodynamic concepts [3,9]. Only lately has experimental confirmation of the essential validity of the above relations been obtained [10]. In this work an analysis and a discussion of the validity of both equations is given. It is, however, difficult to experimentally verify these relations due to the fact that until recently, there were no reliable methods of determining the interfacial tension at the boundary of a solid body.

The above equations have been verified by comparing the values of the work of adhesion. These values were determined experi-

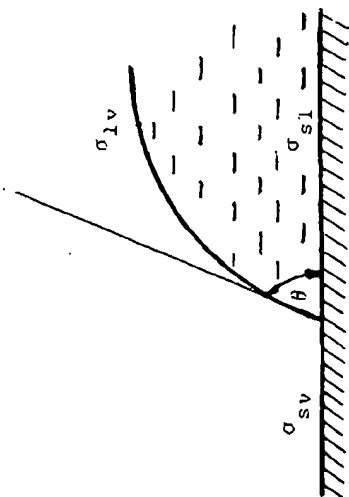


Fig. 1. The contact angle (θ) of wetting the solid surface by the liquid.

mentally by measuring critical slope angles of the solid body surface at which the liquid drop begins to roll off [8,11, and 12] which were calculated from equation (2) and by the experimental data for the contact angle and the liquid surface tension. Connection between the work of adhesion and the slope angle of the solid body surface (α) at which the liquid drop with the mass m and the base radius r begins to roll off is presented by the formula [8,11]:

$$W_a = \frac{mg \sin \alpha}{2r}$$

which has been verified experimentally.

Satisfactory correspondence of the values of the adhesion work on wetting various solid bodies by different liquids (water, mercury, glycerine) confirms the essential correctness of equation (2). Equation (1) can be readily obtained from 2 from the evident relation:

$$W_a = \sigma_{sv} + \sigma_{lv} - \sigma_{sl} \quad (3)$$

(Dupre equation). That is why the correctness of equation (2) confirms the validity of equation (1).

At the same time a number of phenomena complicate the process

of wetting and spreading and make an impression of apparent unsuitability and incorrectness of the equations being considered. These complicating factors include hysteresis of wetting, the solid body surface slope in special cases of wetting (a liquid drop at the inclined surface), deformability of the solid surface, its non-uniformity and roughness and liquid vapor adsorption at the solid surface which decreases the surface tension of the latter. The effect of these factors is considered in [10].

A. Interfacial Surface Energy and Contact Angles of Wetting in Equilibrium and Non-Equilibrium Systems

When a liquid is in contact with the surface of a solid body, the system can be either in thermodynamic equilibrium or not in equilibrium during frequently large time periods. In particular, some high-temperature systems containing metal melts as a liquid phase which can react intensively with solid phases belong to the latter class. Thus, even in non-equilibrium systems, there are interfaces and interfacial surface energies connected with them. Differentiation of various classes of systems has been given little attention in literature up to now. Meanwhile, contact surface processes take place in various systems with inherent peculiarities. Equation (1) and (2) are derived for "equilibrium conditions" (the term which is to be specified in this case). There arises a question about the possibility of applying these equations to non-equilibrium systems.

Classification of the various systems into those in equilibrium and nonequilibrium and analyses of wetting phenomena in each type of system are given in [15].

In equilibrium systems, solid and liquid contacting phases are under conditions of thermodynamic equilibrium; the chemical potential of each component, and the temperature and pressure in each of the phases are the same. The contact of a liquid of a composition with a solid body of b composition at temperature T

for a system having a phase diagram of the "cigar" type (Fig. 2a) can serve as an example for two-component systems as well as for the contact of the pure liquid A with the pure solid body B for the case of mutually immiscible components (Fig. 2b).

If the solid and the liquid phases, which correspond to an equilibrium composition at the given temperature and pressure are

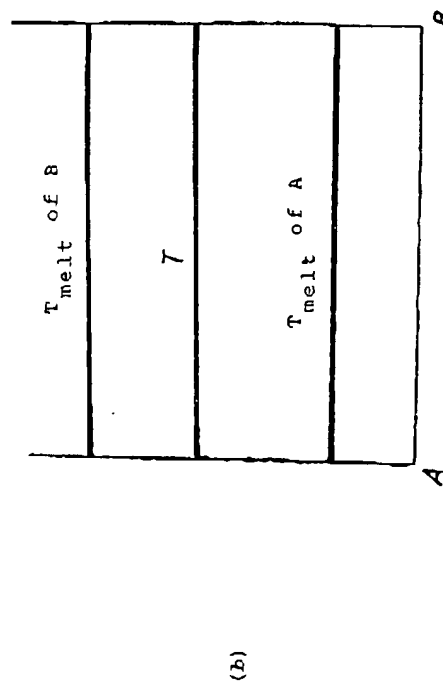
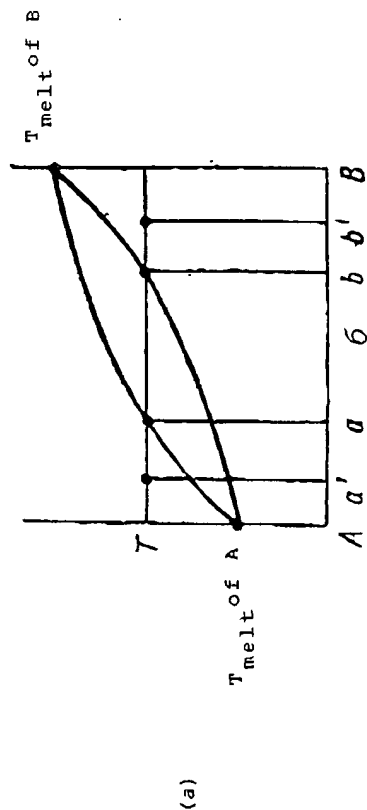


Fig. 2a,b. Types of contact systems (explained in the text)

brought into contact, then the interface between these faces is characterized by a certain interfacial energy and the system remains stable and in equilibrium. When contact between the liquid and the solid body is made, the process of adsorption can be observed at the interface, i.e. transition of some part of the substance into the surface or back but not through the interface.

These processes are characterized by a finite velocity which can be rather small in the case of the solid phase. In the present treatment, instantaneous adsorption is assumed and any non-equilibrium of the system is due to the kinetics of a simple adsorption process and is ignored. At high enough values of the interfacial energy and the liquid phase surface tension, a certain non-zero contact angle of wetting of the solid phase by the liquid is established. The possibility of applying equation (1) to such systems is obvious. The equilibrium angle of contact in this case is accepted to be the wetting angle corresponding to the value determined by this equation.

The interfacial energy σ_{sl} in equilibrium systems depends on nature and structure of the contacting phases and decreases as their properties become increasingly similar.

For non-equilibrium systems one usually considers the case where the system is in thermal and mechanical equilibrium but not in chemical equilibrium. This means that temperature and pressure in each of the phases are the same, but that the components chemical potentials in the solid and the liquid phases may not be equal. Such a situation for a two-component system is presented by the contact of the liquid of composition a and the solid body of composition b (Fig. 2a). After the contact surface appears in such a system, processes will take place which will result in the equalization of the component's chemical potentials in the liquid and solid phases. Such a process could be the transition of one of the components from one phase into another (dissolution, diffusion) or one of several chemical transformations. Whatever the process, the system will shift to an equilibrium state. The interfacial

energy σ_{sl}^* of such a system will change with time and will depend on irreversible processes of chemical interaction at the interface. The action of these processes can result in a substantial interfacial tension decrease. Such a statement has been formulated in a variety of different ways by many authors. Thus A. M. Levin [14], who had studied the stability of refractories in liquid steel and formulated conditions for vigorous wetting of the solid phase by liquid metal, considered that it is necessary for the liquid and solid phases to be as far as possible from equilibrium contact conditions. In the work of Kingery et al. [17,18] and in our study [16,19] it has been found that a metallic liquid will moisten a solid metallic body if a sufficiently intensive chemical reaction is taking place between them.

Let us assume that liquid is chemically adsorbed at the solid body surface. The energy of the bonds formed between the liquid and the solid body is the adhesion work in accordance with the definition of the latter. Binding energy (the work of adhesion) released during the absorption reaction should be equal to the energy of the system, i.e., from the Dupre equation:

$$\sigma_{sl} = \sigma_{sv} + \sigma_{lv} - w_a,$$

it follows directly that growth of the binding energy of the liquid and the solid body (w_a) results in an interfacial tension (σ_{sl}) decrease. Proceeding from this, energy released in the course of the reaction between the solid body and the liquid can be equated to the work of adhesion.

Jordane and Lane [20] pointed to an interfacial energy decrease on wetting solid metals by a liquid phase under nonequilibrium conditions, as a result of a chemical reaction and dissolution. Ono and Kondo [21], have applied the thermodynamics of irreversible processes and obtained the generalized Gibbs formula for interfacial tension under non-equilibrium systems. Apart from the usual factors

* In the general case it is also σ_{lv} .

determining the variation of tension under equilibrium conditions (adsorption and temperature change) the equation includes factors determining interfacial tension change connected with non-equilibrium in the system, for example with the irreversible process of component transition through the interface.

A number of works have been devoted to research into the wettability of solid bodies by metal melts under given deviations of the system (difference of the component's chemical potentials in the liquid and the solid phases) from the equilibrium state [23,24].

Zhukhovitsky et al. [22] have calculated variations of interfacial tension for stationary processes (where a constant difference of the component's chemical potentials in the solid and the liquid phases is maintained):

$$\Delta\sigma = M\Delta\mu$$

where M is a constant. According to this simple relation, the dynamic variation of the interfacial tension is proportional to the difference of the component chemical potentials in the contacting phases. As the system approaches equilibrium, the difference of chemical potential decreases while the interfacial tension increases and stabilizes on reaching equilibrium. In [15] it is shown that for the systems where the solid phase is partially soluble in the liquid phase but the reverse is not true, there should be a minimum in the curve of interfacial tension vs. contact time if pure substances are initially in contact (Fig. 3).

For systems with a layer of a new chemical compound forming at the interface, the melting point of which is higher than the temperature at which the process is taking place, a part of the first downward branch is realized. Evidently, the process is slowed down sharply and is already determined by the component rate of diffusion through the new boundary layer.

Aksay et al. [25] have considered a number of concrete cases of wettability accompanied by chemical interface reactions. The

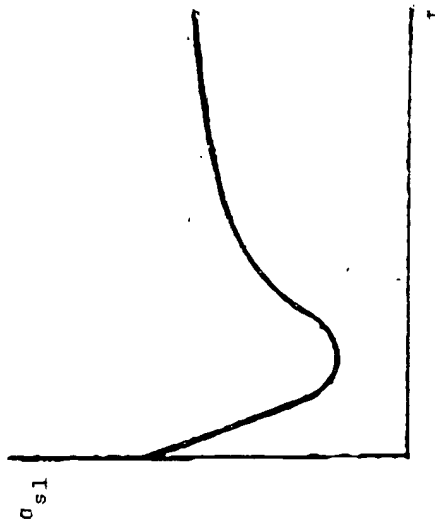


Fig. 3. The curve of interfacial tension as a function of contact time for non-equilibrium systems when the solid phase is partially soluble in the liquid.

curves of interfacial energy change in non-equilibrium systems where the solid phase is dissolving are similar to those in reference [15], and are presented in Fig. 3.

The adhesion work between the two phases 1 and 2 in the general case may be presented in the form

$$W_a = W_a(\text{equil}) + W_a(\text{non-equil}) \quad (4)$$

Interfacial tension is expressed as

$$\sigma_{1,2} = \underbrace{\sigma_1 + \sigma_2 - W_a(\text{equil})}_{\sigma_{\text{equil}}} - \underbrace{W_a(\text{non-equil})}_{\Delta\sigma_{\text{non-equil}}} \quad (5)$$

$$\sigma_{1,2} \approx \sigma_{\text{equil}} - \Delta\sigma_{\text{non-equil}}$$

where σ_{equil} is a function of the difference in the nature and properties of contacting phases P_1 and P_2 : $\sigma_{\text{equil}} = f(P_1, P_2)$ and $\Delta\sigma_{\text{non-equil}}$ is the function of the systems' deviation from the equilibrium state (the differences of the component chemical poten-

tials) $\Delta\sigma_{\text{non-equil}} = \phi(\mu_1^1 - \mu_1^2)$.

Differences of the phase properties are evidently the original reason for a positive interfacial tension. The interfacial tension ($\sigma_{1,2}$) is equal to the value of σ_{equil} for the case when the phases 1 and 2 are under conditions of thermodynamic equilibrium at their contact, i.e. the component chemical potentials in these phases are equal and $\Delta\sigma_{\text{non-equil}} (W_a(\text{non-equil}))$ is zero.

When the phases properties approach each other, $P_1 \rightarrow P_2$, the tension σ_{equil} decreases and, when the phases become identical in the limit, the interfacial tension disappears and $W_a(\text{equil})_2$ equates to the work of cohesion between the phases. At $\mu_1 \neq \mu_2$ the interfacial tension is less than $\sigma_{\text{sl, equil}}$ by the value of energy of the chemical reaction taking place between the phases, $\Delta\sigma_{\text{non-equil}} = W_a$.

It should be noted that the tension decrease due to intensive chemical interaction at the interface can be high, i.e., that $\Delta\sigma_{\text{non-equil}}$ interfacial tension can become negative, i.e. an energy decrease can be observed at the interface. Such a system is considered to be thermodynamically unstable. However if one of the contacting phases is solid, the sluggishness of mass transfer processes in the solid phase can prolong such a situation for a long time (metastable equilibrium). Dependence of σ_{sl} , θ and W_a on time is the characteristic feature of non-equilibrium systems.

The possibility of applying equations (1) and (2) in non-equilibrium systems where σ_{sl} , θ and W_a are the functions of time is discussed in [10] and [15].

One may recognize non-equilibrium spreading by the fact that the initial angle of contact will differ from that at equilibrium as determined by equation (1) (usually $\theta_{\text{init}} > \theta_{\text{equil}}$), but gradually assumes the equilibrium value. The dynamic force of spreading is

$$P = \sigma_{1v} (\cos \theta_{\text{equil}} - \cos \theta t)$$

where θt is the value of wetting angle at the given moment of time.

Liquid inertia and viscosity are the forces which inhibit spreading. For liquid metals with low viscosity the process of spreading takes place at high speed since the variation of the angle of contact from about $180-160^\circ$ to $30-50^\circ$ occurs during approximately 10^{-2} seconds [26]. During the whole period of spreading, the application of (1) and (2) is evidently meaningless. For similar systems a process of slow spreading is also possible ("equilibrium" or quasi-static spreading). This can be frequently observed in metal melts* due to the change with time of the interfacial tension (σ_{sl}). The change in σ_{sl} is in turn due to the chemical contact reaction or diffusion at which the inertial forces and the liquid phase viscosity are small and equilibrium of surface forces is gradually realized during the process. For this latter case equations (1) and (2) are valid and by measuring the instantaneous contact angle value one can calculate the corresponding value of the interfacial energy and the work of adhesion.

B. The Nature of Adhesive Forces Determining the Wettability of a Solid by a Metal Melt

The wettability of a solid body by a liquid and the bond between the liquid and the solid body is determined, just as in adsorption, by two types of forces acting between the phases: (1) physical interactions which combines polarization and dispersion forces; (2) chemical forces, both ionic and homopolar. The basic difference, of significance here, between these two types of forces is their magnitude. The bond energies of physical (van der Waals) forces are functions or units of a kcal/mole. The energies of chemical interaction equal tens and hundreds of kcal/mole.

*The authors [55] have observed the reduction of the contact angle of a copper-aluminum liquid alloy wetting uranium dioxide from 140 to 80° over a period of several hours. The contact angle of graphite wetting by stannus-titanium melts decreases to a stable value over 2-4 hours [40].

Taking into account that the surface tension of most metals (excluding alkali metals) is of the order of 10^3 erg/cm², for spreading, or a significant degree of wettability, by a liquid metal on any solid body, the energy of interaction (the work of adhesion of the metal with the solid body) is of the same order of magnitude, i.e., 10^3 erg/cm². Taking the adhesion work to have this value

$$W_a(\text{mol}) = W_a \cdot S_M' \cdot S_M = \left[\frac{M}{\rho} \right]^{2/3} \frac{1}{N^{1/3}} \quad (7)$$

(where M is the solid material molecular weight, ρ is density, N is Avogadro number, S_M is the area occupied by a mole of substance if it is extended into a monoatomic film) we shall obtain for W_a (mol) a value of tens of kcal/mole. Physical forces cannot provide such energy; this energy can be obtained by chemical interaction. Physical (dispersion) forces determine the wettability of liquids with low surface tension (water, organic solvents and so on) for which σ_{lv} and W_a constitute tens of dyne/cm. The distinguishing feature of "chemical" wetting, apart from the large value of interphase forces, is a comparatively strong dependence of the degree of wettability on temperature. Such dependence is often characterized by a "wetting threshold", i.e. by the presence of a temperature beyond which the contact angle begins to decrease sharply and the work of adhesion begins to increase. The character of the change of $W_a = f(T)$ can evidently in some cases be a characteristic by which this or that system can be related to a certain class. For systems with physical wetting it is possible to establish the connection between the degree of wetting and other properties of contacting materials, such as polarizability, ionization potential, dielectric constant, etc.

In the case of wetting determined by chemical interaction, it is necessary to allow for variables characterizing the chemical affinity of atoms from different phases, the difference of the component chemical potentials in phases, the reaction equilibrium constant, the free energy of formation of the compounds, etc. In con-

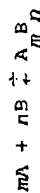
nection with the characteristic feature of wetting in non-equilibrium systems (namely, its irreversibility) only the wetting angle of infiltration makes any sense.

The process of irreversible wetting can be described in turn within the framework of the thermodynamics of irreversible processes. The latter is developed today only for partially suitable cases (small deviations of the system from the equilibrium state, stationary processes). That is why in the present work, the usual thermodynamic interpretation of wetting as a chemical process reaching equilibrium (pseudo-equilibrium) in the near-contact layer is accepted and applied as far as possible.

1. The Determination of W_a (non-equil) values

The interaction energy W_a (non-equil) can be approximately calculated using thermodynamic concepts. Let us consider this approach for the contact between the solid body and the liquid.

Let the atomic plane of the solid phase A with a surface density of N_A moles/cm² be in contact with the atomic plane of the liquid B containing N_B moles/cm². Let the reaction



take place in the system A - B.

Keeping in mind that the surface energy is localized within a very short distance of the immediate surface of the substance, let us restrict ourselves to considering the interaction of atoms of only the first contact planes of the substance A and B which form. In accordance with Guggenheim [28,35] treatment, this is the surface phase. Let us calculate the energy released by the reaction taking place in this phase between n_A moles of A and n_B moles of B as the initial state (a mixture of n_A moles of A and n_B moles of B) to form the final equilibrium state in this phase characterized by the presence of all three substances A, B, and A_mB_n .

The concentrations of these substances, at any moment of time, can be expressed as functions of n_A , n_B and α where α , the degree

is the number of A B moles formed.

As it is easy to see for the given reaction equation

$$C_A = \frac{n_A - m\alpha}{n_A + n_B + \alpha(1-m-n)}; \quad C_B = \frac{n_B - n\alpha}{n_A + n_B + \alpha(1-m-n)}$$

$$C_{\text{A}_m\text{B}_n} = \frac{\alpha}{n_A + n_B + \alpha(1-m-n)}$$

In the initial state $\alpha = 0$, at equilibrium $\alpha = \alpha_0$ the energy variation accompanying the transition from any intermediate state at a given α to the equilibrium one, so that an infinitesimal number of reactants will take part in the process and an infinitesimal number of reaction products will be formed, is evidently expressed in the following way (reaction isotherm):

$$dZ = \left(RT \ln \frac{C_A^m C_B^n}{C_{\text{A}_m\text{B}_n}} - RT \ln \frac{C_A^m C_B^n}{C_{\text{A}_m\text{B}_n}^0} \right) d\alpha, \quad (8)$$

where the superscript 0 refers to the equilibrium state.

The total work of reaction equal to the adhesion work is expressed as:

$$W_a = \Delta Z = \int_0^{\alpha_0} dZ \quad (9)$$

After integrating we shall obtain an expression for ΔZ as a function of α_0 . The former is found from the expression for the constant of the reaction equilibrium

$$\Delta Z^0 = -RT \ln K = RT \ln \frac{C_{\text{A}_m\text{B}_n}^0}{C_A^m C_B^n} \quad (10)$$

where ΔZ^0 is the standard change of isobaric potential.

Thus for calculating W_a (non-equil) it is necessary to know the following characteristics of the system: n_A , n_B , the approximate mechanism of reaction and how the standard isobaric potential ΔZ^0

changes. Calculation of these formulae for different systems has been done in [10] and is also presented below.

2. The Value of $W_a(\text{equil})$

The value of $W_a(\text{equil})$ for systems with a high energy of interatomic bonding in each of the phases and a high surface energy (metals, high melting chemical compounds) can be written in two separate parts:

$$W_a(\text{equil}) = W_a(\text{chem.equil}) + W_a(\text{VDV})$$

Here $W_a(\text{chem.equil})$ is the cohesive energy of the solid and the liquid phases due to establishment of chemical equilibrium bonds, i.e. due to the mutual saturation of the free valences of the contacting surfaces. The establishment of such bonds is not accompanied by rupture or partial dissociation of interatomic bonds in each of the phases (the process characteristic for chemical irreversible interaction) taking place in non-equilibrium systems; $W_a(\text{VDV})$ is the energy of van der Waals (physical) interaction (dispersion bond).

For many systems where the phases present differ in their nature (liquid metals, non-metal crystals: ionic compounds, covalent substances and compounds) the value of $W_a(\text{chem.equil})$ is rather small (there is little or no saturation of surface valences). Against a background of weak chemical interaction, dispersion binding forces become pronounced; the low total value of the experimentally observed work of adhesion for these systems can be explained by the energy of dispersion interaction forces. This energy can be numerically estimated for some systems. For this purpose one can use the expression for the potential or dispersion interaction between a pair of atoms:

$$E = \frac{1}{2} \frac{\alpha_1 \alpha_2}{R^6} \cdot \frac{I_1 \cdot I_2}{I_1 + I_2}, \quad (11)$$

where α_1 and α_2 is polarizability; I_1 and I_2 are the first ionization potentials of atoms 1 and 2 and R is distance between them.

Neglecting entropy contributions and taking into account only interactions between each pair of atoms, we shall obtain $W_a(\text{equil}) = nE$ where n is the number of substance atoms/cm² of the surface area. Calculations of the energies of binding dispersion forces for the contact of solid bodies and liquid metals have been published in works by Benjamin and Weaver [29], MacDonald and Eberhart [30] and the author [10]. Knowing $W_a = W_a(\text{equil}) + W_a(\text{non-equil})$ one can, with the help of equation (2) find the angle of contact.

III. METHODS OF MEASURING THE WETTABILITY OF A SOLID BODY BY A LIQUID METAL

The main characteristics of the contact capillary system (solid body, liquid and gas) are the angle of contact of the solid phase wetting by the liquid and the surface tension of the latter.

This chapter deals with a number of methods for determining these values applied to high-temperature metal melts. The sessile drop method and the plate weight method are most suitable for this purpose.

A. Sessile Drop Method

The first law of capillarity, a general differential equation determining the form of the liquid surface in the gravity force field for the case of the liquid drop resting on the horizontal solid surface and being the surface of revolution (Fig. 4), can be expressed in the following way [32]:

$$\frac{1}{\rho/b} + \frac{\sin \phi}{x/b} = 2 + 2/b \frac{(D-d)gR^2}{\sigma_{lv}} \quad (12)$$

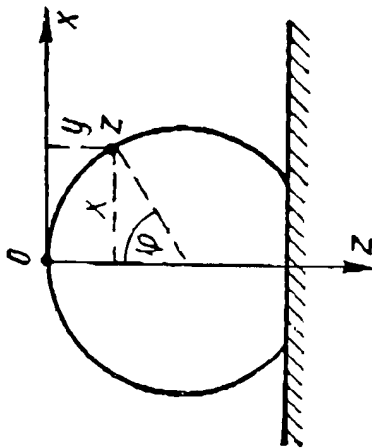


Fig. 4. Coordinates of the point at the liquid drop surface.

where ρ is the radius of the surface curvature in the plane of its meridional section (the plane of the drawing); b is the radius of the drop surface curvature at its top ($R_1 = R_2 = b$); expression

$$\frac{(D-d)gb^2}{\sigma_{lv}}$$

is denoted by β ; $D-d$ is the difference between the

densities of the liquid and the medium (the latter can be neglected for a liquid-gas phase system); g is gravitational acceleration; x and z are coordinates of a point on the liquid surface.

The solution of this equation relates the point coordinates on the surface x, z, ϕ with the liquid surface tension at the interface with the medium σ_{lv} , the liquid density (difference of the liquid and medium densities) and the gravitational acceleration. By measuring the point coordinates at the liquid drop surface one can express the liquid tension through its density. From the equation solution one can also find the liquid surface inclination at any point including the point of contact with the solid surface, i.e. the contact angle of wettability.

Thus the sessile drop method allows us to determine the values of σ_{lv} and θ . Having the equation of the liquid surface shape, it is possible to determine the volume enclosed in it, i.e. the drop volume, and hence to determine the liquid density. Though the

solution of equation (12) cannot be presented in the definite form nevertheless its integral can be obtained approximately with a known degree of accuracy.

There are different methods of approximate integration of equation (12) (the list of approximate formulae is given in [4, 31, 32], those for graphical integration including [36]). The most accurate solutions of this equation (for figures of revolution) are the tables obtained in the work of Bashforth and Adams [34].

The formula for calculating σ is of the form

$$\sigma = \frac{gub^2}{\beta}, \quad (13)$$

where b and β are determined from Bashforth's and Adams's tables [34] by the measured coordinates x, z, ϕ . Measurements of x and z are usually carried out at the selected ϕ , most often (if $\phi > 90^\circ$) at $\phi = 90^\circ$. Such measurements are the most accurate ones.

Measurements of $\phi < 90^\circ$, which are obtained with good substrate wetting by the liquid, are less accurate, but, on observing special measures, they can also yield good results.

To determine the values of the x, z and ϕ coordinates of the drop contour, the image of the latter is photographed (the print should be of very high quality). Judging by the print, the maximum drop diameter ($2x$), the distance to the apex z at $\phi = 90^\circ$ are determined with the measuring microscope.

There are other methods of measuring photographs [37]. From the photograph, one can either calculate the angle of contact using Bashforth's and Adams's tables, or directly measure it by drawing a tangent to the drop contour near the wetting perimeter.

Apart from the ordinary method of drawing a tangent to the drop contour, the angle of contact can be calculated from the drop dimension (height b and diameter of the wetting perimeter $2a$) by the formulae for spherical segment (assuming that the drop surface is spherical, an assumption which is valid for sufficiently small

drops):

$$\operatorname{tg} \theta = \frac{2ha}{a^2 - h^2} \quad (14)$$

or from the drop volume and height

$$\cos \theta = 1 - \frac{3\pi h^3}{3v + \pi h^3} \quad (15)$$

In several variants those methods were applied in the works by Ferguson [33], Volkova [39], Bikerman [40], Wolfram and Weber [41] and Levin [14].

If the drop is rather large so that its curvature at the apex can be neglected, the angle of contact is determined by the expression

$$\cos \theta = 1 - \frac{Dgh}{2\sigma_{lv}} \quad (16)$$

The above formula is valid only for rather large liquid drops (diameter of 5-10 cm and more) [33].

The sessile drop method has some advantages which are of great importance while working with melted metals. They are principally the simplicity of the method, the need for only small quantities of material for the liquid and solid phases (the liquid phase quantity may sometimes constitute even less than 10^{-2} - 10^{-4} g.) and the single shape of the solid body. This method does not require direct access to the sample during measurements which can be conducted at substantial distances from the object so that the latter can be placed in a special closed apparatus, to be heated and so on. The main disadvantage of the method consists in non-reproducibility of the liquid surface which accumulates contaminants and impurities.

Nevertheless, this disadvantage can be eliminated by observing special precautions and carrying out the test carefully with highly purified materials.

B. The Plate Weight Method

The essence of this method is as follows. The plate, partially submerged in the liquid, is subject to an additional capillary force tangential to the plate surface and normal to the wetting perimeter [38, 43]. This force can be expressed by projecting the vector of the liquid surface tension near the wetting perimeter onto the plate plane

$$f = \sigma_{lv} \cos \theta \cdot l$$

where l is the wetting perimeter length.

The origin of this force can be understood from the following simple considerations. In Fig. 5 a plate is shown submerged in a liquid. The plane of the diagram intersects the plane normal to the plate plane and that of the liquid surface. The free energy of such a system can be expressed as

$$F(x) = 2b(H-x)\sigma_{sv} + 2b\sigma_{sl} + S_{lv}\sigma_{lv} + \phi \quad (16)$$

where x is the depth of the submerged plate, H is the plate height, b is its width (the thickness is assumed to be negligible), S_{lv} is

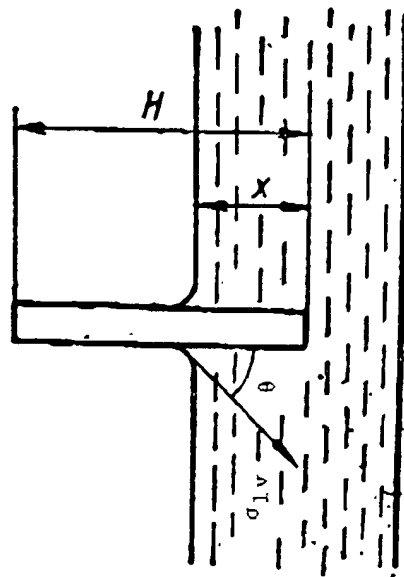


Fig. 5. The derivation of the force equation for the plate immersed into a liquid.

the liquid surface area which borders on the gas phase, ϕ is the volumetric contribution to free energy. The plate weight is not taken into account for simplicity. Then the projection of the capillary force in the x direction is determined by

$$f_x = \frac{\partial F(x)}{\partial x} = 2b(\sigma_{sv} - \sigma_{sl}) = -2b\sigma_{lv} \cdot \cos \theta$$

In practice it is necessary to allow for archimedean force and make corrections for edge effects.

Using the plate weight method one can immediately obtain the contact angle value averaged over the whole wetting perimeter, which is rather large in this method (about 2-3 cm).

Really, according to this method, the total force which pulls in or pushes out the plate is

$$f = \sigma_{lv} \int \Delta l_i \cos \theta_i$$

where Δl_i is the wetting perimeter section along which the angle of contact maintains the constant value θ_i .

The angle of contact being measured is obviously determined by the expression:

$$\cos \theta = \frac{\sum \Delta l_i \cos \theta_i}{l}$$

where $l = \sum \Delta l_i$ is the wetting perimeter length.

C. Instrumentation for Measuring Surface Tension and Wetting Angle

The main requirements for measuring surface tension and wetting angles by the sessile drop method in the placement of a symmetrical drop of the melt on the solid surface under study (the substrate) are: a horizontal position of the surface, an enlarged image, as clear as possible, of the melted drop profile and solid substrate parallel to the surface of material being studied. The sample should be in a controlled gaseous atmosphere or in a vacuum at the temperature specified.

These requirements are met by means of devices including the bumping system (vacuum system), the temperature control and the photooptical system. The latter should have a considerable number of degrees of freedom in arranging the components in order to carry out different adjustments of the system.

A standard apparatus for studying the wettability of solid bodies by liquid metals using the sessile drop method is shown in Fig. 6. The vacuum chamber of the apparatus is a steel vessel with a volume of about 15 liters which encloses a horizontal tubular furnace with a sample. The chamber is evacuated down to the pressure of 10^{-5} to 10^{-6} Torr. The pump exhaust is connected to the line of preliminary rarefaction made of stainless steel tubes with 100 mm diameter and evacuated by a rather powerful forevacuum pump removed from the laboratory room to a special compartment. The experience of such forevacuum lines operation demonstrated their reliability and convenience.

Since getting the apparatus into working order (obtaining the needed vacuum at the required high temperature) takes a considerable time, the apparatus includes a device which permits the changing of samples in the furnace at the working temperature without breaking vacuum.

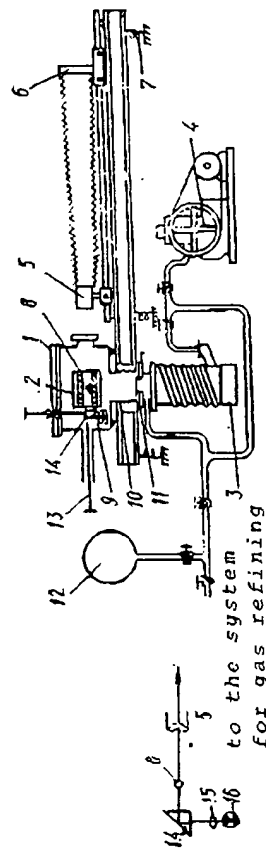


Fig. 6. Scheme of the apparatus for determining surface tension and wetting angles of metallic liquids. 1-vacuum chamber; 2-furnace; 3-steam-oil pump; 4-backing pump; 5-objective; 6-cassette portion; 7-springs; 8-metal sample on the substrate; 9-next samples; 10-bellows; 11-vacuum valve; 12-tanks for purifying inert gases; 13-horizontal rod; 14-quartz prism; 15-condenser; 16-light source; 17-vertical rod.

Apart from high efficiency for sample handling that such a device provides, it is especially important for studying metals with high chemical activity. Using this device it is possible to heat and degas the apparatus and the furnace components, to obtain the necessary vacuum and temperature (the sample is contained in a special compartment out of the furnace in a cold state and does not interact with residual gases) and only then to introduce the sample under study into the furnace space.

Other modifications provide for batch delivery of the various melts directly to the drop (introducing additives into the drop during the test without breaking vacuum [44]), for the liquid metal drop penetrating the solid surface under study [45], and for touching the drop top (melted on the neutral additional substrate) with the surface of a solid phase under study and establishing the contact angles near this surface [46]. The latter procedure was used to study the kinetics of spreading [26].

Attachment lens of different types permit shooting the spreading process at frame frequencies from 16 to 3000 per second.

The whole assembly (optical bench and camera) is mounted on a solid frame placed on damping springs ("floating" structure) protecting the assembly from vibration which deteriorates the drop contour definition on the print and distorts it. For operation in an inert atmosphere a system for gas refining and drying is incorporated.

The ordinary sessile drop method for determining metal surface tensions is not accurate enough. The measuring error reaches 5 per cent. That is why, while studying such processes as the variation of surface tension with temperature, the magnitude of which is rather small, this method is not applicable.

An improved version of the sessile drop method has been developed and is called the "large drop" method [42]. Here a metal drop of a rather large size is formed at the edge of the flat crucible, "a cup" with sharp edges forming a circle of the required diameter (usually 10 to 20 mm) (Fig. 7). The base of the drop

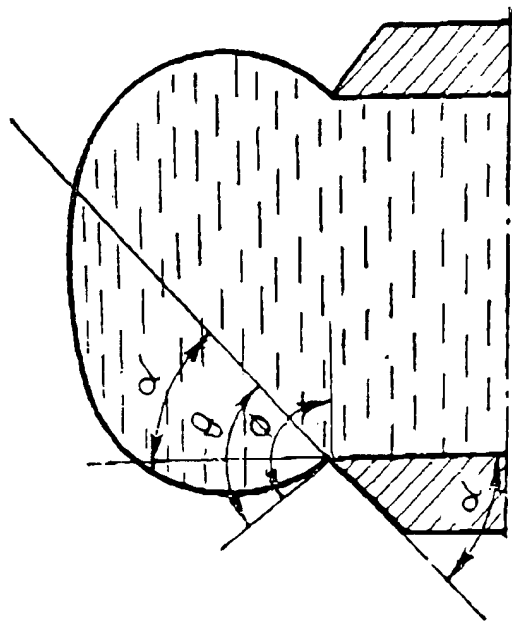


Fig. 7. Liquid drop in the cup ("large drop" method).

takes the form of the cup edge and is symmetric (circular). This produces a strictly symmetrical form of the drop and results in high accuracy and reliability with this method (errors are about 0.3 to 0.5%).

An analysis of the methods of exactly measuring the contact angles and the effect of various factors (posity and roughness of the surface, its slope, etc.) is given in reference [10].

An increase in the surface roughness results in a corresponding increase in the contact angle (infiltration angle). For quartz glass wetting by copper and tin the transition from a polished to a roughly-polished surface for the solid phase causes the contact angle to grow by 17 to 18° [10]. In other work [250] still greater growth of the contact angle was observed for liquid aluminum on the smooth ($\theta = 53$) and rough ($\theta = 114$) surface of titanium nitride and on the smooth ($\theta = 67$) and rough ($\theta = 129$) surface of titanium diboride. In the latter cases evidently an additional effect is superimposed on that of the rough surface. On observing necessary

hygienic conditions for the experiment, on having a solid substrate with a high degree of smoothness and maintaining a true horizontal position, errors in determining the contact angle do not exceed 1 to 2°.

IV. THE WETTABILITY OF DIFFERENT CLASSES OF SOLIDS BY LIQUID METALS

While studying and analyzing wettability phenomena in well-defined systems, it is expedient to divide the latter into a number of classes in accordance with the physico chemical nature of the solid phase: (1) Metal melt - ionic compound (high-melting metal oxides, salts), (2) Metal melt - substance or compound with preferably covalent character interatomic bonding (diamond, graphite, carbide, nitride phases), (3) Metal melt - high-melting metals or metal-like compounds. In the first two types of systems, solid bodies are characterized by a closed stable electronic configuration or atoms, and strong saturated interatomic bonding. Interaction of most solid bodies of these types with metals is possible only with partial or complete dissociation of the interatomic bonding in the solid bodies. Such solid bodies are somewhat less reactive than metal melts. With solid bodies, a key feature in systems of the first type is the large size of anion and its high polarizability as compared to cation. In ionic bodies, the surface is formed by anions, and their interaction with metal melts is determined mainly by the interaction with the solid body anions.

In the third type of system, the establishment of equilibrium interphase metal bonds with surface atoms is possible without dissociating bonds within the solid phase. Wettability in these systems is greater than with the first two.

The characteristics of wettability in each type of contact systems are set out below.

WETTABILITY OF SOLIDS BY LIQUID METALS

A. The Wettability of Ionic Compounds by Metal Melts

Those systems formed by high-melting metal oxides are of the highest practical value. Interatomic bonds in these compounds are essentially of ionic nature.

High-melting metal oxides are as a rule poorly wetted by liquid metals. So contact angles of mercury, tin, lead silver, copper, nickel, cobalt, iron and platinum on high-melting oxides of aluminum, magnesium, silicon and beryllium are of the order of 120 to 150°. However even the initial qualitative observations of metal-oxide contact have shown that some metals (titanium, zirconium, barium, aluminum and so on) intensively wet the oxide surfaces [17,47-51]. The factors which govern the phenomenon of oxide wettability by liquid metals have been obscured for a long time.

Weyl [52] considered that metals which are able to form highly charged ions (Sn^{+4} , Al^{+3}) should wet ceramic surfaces better due to an enhanced electrostatic interaction. Kingrey also thought that formation of high charge metal ions would be favorable for metal-ceramic binding. The idea of purely electrostatic metal-oxide binding was also supported by Cabrera and Mott [54] and Livey and Murray [55] who felt that this interaction was essential in metal systems.

While we do not completely neglect such a binding mechanism, it should be noted that it is not the basic one. One can give many examples when it is not possible to explain the wetting phenomena being observed in these terms. Thus, barium (Ba^{+2}) wets and impregnates aluminum ceramics as well as aluminum [47]; sodium (Na^{+1}) spreads over glass [56] and uranium dioxide [55]; silver (Ag^{+1}) spreads over copper oxide [48]. Tin, which according to Weyl has great affinity to oxides, does not actually wet high-melting oxides (Al_2O_3 , MgO , ZrO_2 , etc.) as accurate quantitative study has shown. According to [54] and proceeding from electrostatic theory, metals in general should effectively wet oxides since the latter are polar. In reality quite an opposite picture is observed.

Brace [49] and Bondi [56] tried to explain the wettability of

oxides by some liquid metals. They supposed that the liquid metal reduced the solid oxide surface layer to the metal, and that the latter was well wetted by the metal melt. This explanation is important in that it points out potential wetting process chemistry in oxide-metal systems.

As a result of studying wettability and contact interaction between oxides and various liquid metals the following important features have been established:

(1) On the basis of the works of Kingrey et al. [17,18,53,57, 61-65], this author and Eremenko [16,19,95], Popel et al. [68,72-76], Armstrong et al. [66,67] and other studies [29,59,60,77,79, 80-83,102,103] it can be stated that wettability of oxide by a metal and adhesion in such a system increases with growing affinity of the liquid phase metal for oxygen. This is indicated by variations in the thermodynamic potential of metal oxide formation (ΔZ).

Chemically oxygen-active metals such as titanium, zirconium, aluminium, silicon, manganese and lithium (either pure or in the form of alloys) form small contact angles and spread completely over certain oxide (Al_2O_3 , BeO , SiO_2 , MgO) surfaces.

In some works [110,111], a natural decrease of the wettability of some oxides (V_2O_5 , Al_2O_3 , SiO_2 , TiO_2) by iron, nickel, cobalt, aluminium, silicon and tin is accompanied by an increase in the free energy of metal oxide formation. However such dependence allowing only for the properties of one component of the contact pair (the metal) is one sided. It is obligatory to take into account the properties of the other component (the oxide) as well.

(2) On the basis of general considerations, it can be expected that interaction of any substance with a chemical compound will be the less intensive the stronger the intramolecular bonds are. Thus one may consider that the weaker the bonds between the metal and the oxygen in the oxide, the greater the chemical interaction and the wetting of oxides by metals should be.

Research into the wettability of binary oxide phases-solid solutions by metal melts [10,19,71,83] depending on their composition

has established a general correlation between the value of the oxide's electrical conductivity (its intrinsic conductivity), its thermodynamic stability or free energy of formation, i.e., the strength of the metal-oxygen bond, and its wettability by a metal. Compounds with a smaller free energy of formation, formed from the metal and oxygen (which have, as a rule, higher electrical conductivities), are better wetted by liquid metals [81,10] (Fig. 9).

Similar dependences of wettability on the composition of the oxide solid solutions have been obtained by Tikkonen [71]. Data on the growth of the wetting contact angle of the oxide by the liquid metal with increasing bond ionicity [112] and on the oxide space lattice energy [110,111] are in agreement with the above correlation.

It is, however, necessary to allow for the following circumstances. The surfaces of the highest-melting oxides are formed by oxygen anions of large size. Metal cations of smaller size are displaced from the surface and move to the interior of the oxide. In the process of formation of a fresh ionic crystal surface, ions

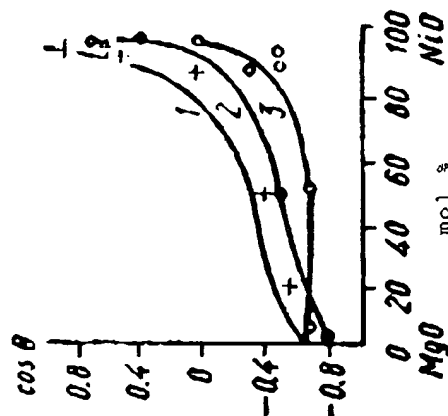


Fig. 8. Wettability by metal melts of binary oxide phases (solid solutions magnesium oxide-nickel oxide) depending on the composition: 1-tin; 1000°C; 2-copper; 1200°C; 3-silver; 1100°C.

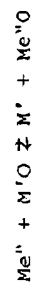
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of the boundary plane affected by the vector field of the bulk ions move deep into the crystal in a direction normal to its surface. Due to the different size and polarizability of the various kinds of ions the extent of their penetration varies. Madelung [84] was evidently the first to pay attention to this phenomenon which was also discussed in [85]. Metal ions polarizability is much lower than that of oxygen. The polarizabilities of the ions Mg^{+2} and Al^{+3} for instance are $0.094 \cdot 10^{-24}$ and $0.052 \cdot 10^{-24} \text{ cm}^3$ (according to Pauling); oxygen ion polarizability (O^{-2}) is $3.88 \cdot 10^{-24} \text{ cm}^3$. This circumstance and the relatively large size of the anion lead to the fact that displacement of the surface oxygen ion under the influence of a large crystal field deformation is smaller than that of the metal ion. According to Weyl [86] the oxide surface structure is of the form presented in Fig. 9.

On the basis of these facts, one can state that chemical interaction between a liquid metal and an oxide surface is essentially a metal interaction with the oxygen of the oxide, which can be written as follows:



The change in the thermodynamic potential due to this reaction is:

$$\Delta Z = \Delta Z'' - \Delta Z'$$

where $\Delta Z''$ and $\Delta Z'$ are the thermodynamic potential changes associated with the oxidizing reaction of the liquid metal and the metal forming the solid oxide.

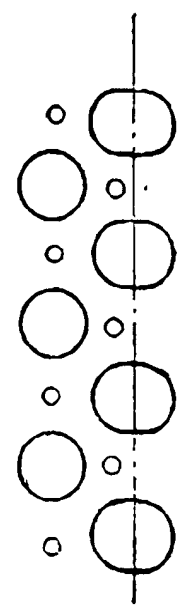


Fig. 9. The surface structure of high-melting oxides.

Just as the degree of solid oxide wettability by the liquid metal is to be associated with ΔZ , the contact angle and the work of adhesion (to be more exact, the non-equilibrium part of the work of adhesion $W_a(n.-eq.)$) should also be associated with ΔZ . The results of comparing wettability and thermodynamic properties of contacting components ΔZ are presented in Fig. 10 and Table 1. In spite of data scattering there is a distinct tendency for θ to decrease with decreasing ΔZ absolute values.

At high positive values of ΔZ , the intensity of metal-oxide chemical interaction is low while contact angles are large. In this case, however, for the more stable inert systems, (Pt-BeO, Pt- Al_2O_3 , Au-BeO for instance (Table 1)), angles of contact are other than 180° , i.e. the adhesion work has a finite value and is 10^1 to 10^2 erg/cm^2 (fractions and whole units of kcal/mol).

One can assume that this energy arises from van der Waals dispersion interactions which, being universal, take place in all

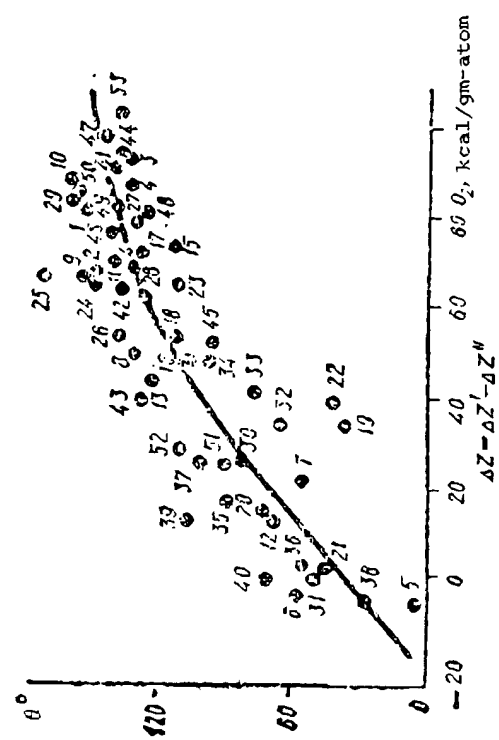


Fig. 10. Correlation between the degree of wettability (wetting angle) and the difference of affinity to oxygen of the liquid phase metal and the solid phase oxide metal. The digits correspond to the system numbers from Table 5.

TABLE 1. The wettability of various oxides by liquid metals and the difference of free formation energies of the solid phase oxide and of the oxide formed by liquid metals

No	System	t °C	θ	$\Delta Z = \Delta Z'' - \Delta Z'$ kcal g. atom O	References
1	2	3	4	5	6
1	BeO-Ni	1500	152	82	[18]
2	BeO-Fe	1550	147	64	[18]
3	BeO-Pt	900	132	92	[10]
4	CaO-Fe	1550	132	72	[14]
5	CoO-Sn	900	0	7	[10]
6	CoO-Ni	1500	58	4	[10]
7	Fe ₃ O ₄ -Cu	1200	57	22	[10]
8	MgO-Fe	1550	130	49	[18]
9	MgO-Ni	1550	152	65	[18]
10	MgO-Cu	1150	160	89	[18]
11	HgO-Sn	1100	139	70	[10]
12	NiO-Cu	1200	68	12	[10]
13	SiO ₂ -Ni	1500	125	44	[10]
14	ThO ₂ -Ni	1500	132	86	[18]
15	ThO ₂ -Fe	1550	111	71	[18]
16	ZnO-Ag	1000	106	48	[55]
17	ZrO ₂ -Ni	1500	130	55	[18]
18	ZrO ₂ -Fe	1550	111	52	[18]
19	BeO-V	1800	35	34	[10]
20	ZrO ₂ -Si	1450	71	13	[18]
21	UO ₂ -Al	1100	46	2	[55]
22	UO ₂ -Na	500	40	39	[55]
23	UO ₂ -Sn	1100	110	64	[55]
24	Al ₂ O ₃ -Ni	1500	150	67	[10]
25	Al ₂ O ₃ -Sn	1100	174	66	[57]
26	Al ₂ O ₃ -Fe	1550	141	53	[64]
27	Al ₂ O ₃ -Pb	900	132	77	[10]
28	Al ₂ O ₃ -Co	1500	125	62	[48]
29	Al ₂ O ₃ -Cu	1100	155	82	[10]
30	Al ₂ O ₃ -Si	1450	82	25	[18]
31	Al ₂ O ₃ -Al	1250	48	0	[55]
32	Al ₂ O ₃ -Cr	1900	65	35	[10]
33	BeO-Si	1450	76	41	[18]
34	BeO-Cr	1900	100	48	[10]
35	Cr ₂ O ₃ -Fe	1550	88	16	[10]
36	Fe ₃ O ₄ -Sn	1000	52	4	[10]
37	MgO-Si	1450	101	20	[18]
38	NiO-Sn	1000	27	7	[10]
39	TiO ₂ -Si	1450	107	13	[18]
40	CoO-Co	1500	70	0	[71]

Table 1 (continued)

No	System	t °C	θ	$\Delta Z = \Delta Z'' - \Delta Z'$ kcal g. atom O	References
1	2	3	4	5	6
41	CaO-Ni	1500	135	92	[71]
42	SiO ₂ -Cu	1100	134	62	[10]
43	SiO ₂ -Sn	900	127	40	[10]
44	BeO ₂ -Pt	1780	125	92	[10]
45	ThO ₂ -Cr	19000	92	52	[10]
46	SiO ₂ -Au	1100	140	75	[10]
47	Al ₂ O ₃ -Au	1100	138	98	[10]
48	UO ₂ -Cu	1100	125	80	[79]
49	UO ₂ -Bi	700	140	82	[69]
50	UO ₂ -Bi	700	155	85	[69]
51	UO ₂ -Si	1420	90	26	[55]
52	CdO-Ag	970	112	27	[55]
53	MgO-Ag	1235	136	102	[55]

systems. The energy of this type of interaction can be evaluated. The order of magnitude (usually several kcal/mol) of the energy of these forces can be compared with the observed work of adhesion for systems with a low degree of wettability.

Wettability increases as ΔZ positive values decrease, the trend continuing as ΔZ assumes negative values.

A number of pure elements or additions to inactive metals, having a high affinity for oxygen, effectively wet oxide materials. One of the metals which has been extensively studied and used in practice is titanium. The wettability of oxides by titanium-containing melts Cu-Ti, Au-Ti, Ni-Ti, Ga-Ti, Sn-Ti and so on, has been investigated in a number of works [57,79,82,101-103,105,179]. Some data are summarized in Tables 2 and 3 and in Fig. 11. A sharp decrease in the contact angle at low elemental concentrations is a characteristic feature for titanium and its alloys which are interfacially active (Fig. 11). Because of influence of adsorption, the titanium concentration at the liquid phase-solid oxide interface is much higher than that within the

TABLE 2. Contact angles for titanium containing melts on high melting oxides.

System	Temperature °C	contact angle (degree), Ti content, % (at.)										
		0	1	2	3	4	6	8	10			
Au-Ti-Al ₂ O ₃	1150	135	100	90	81	76	69	66	64			
Au-Ti-Ti ₂ O ₃	1150	113	96	85	77	72	67	65	-			
Cu-Ti-Al ₂ O ₃	1150	129	88	50	40	32	21	14	-			
Cu-Ti-Al ₂ O ₃	1150	148	108	58	40	32	21	14	-			
Cu-Ti-MgO	1150	133	95	61	43	36	26	-	-			
Cu-Ti-SiO ₂	1150	128	72	45	40	35	27	-	-			
Cu-Ti-TiO _{1.86}	1150	72	67	61	55	49	40	31	-			
Cu-Ti-Ti _{1.14}	1150	82	75	68	63	58	48	40	-			
Cu-Ti-Ti ₂ O ₃	1150	113	90	62	45	32	21	15	-			
CuAg(28:72)-Ti-Al ₂ O ₃	980	118	91	85	-	-	-	-	-			
Ni-Ti-Al ₂ O ₃	1500	110	104	99	95	92	87	83	77			
NiMo(58:42)-Ti-Al ₂ O ₃	1500	114	97	86	77	71	66	64	62			
Sn-Ti-Al ₂ O ₃	900	131	80	79	70	67	60	-	-			
Sn-Ti-Al ₂ O ₃	1000	127	71	65	60	56	48	-	-			
Sn-Ti-Al ₂ O ₃	1150	127	60	49	44	42	38	35	-			
Sn-Ti-SiO ₂	900	132	60	50	42	35	27	-	-			
Sn-Ti-SiO ₂	1000	127	52	36	26	18	10	-	-			
Sn-Ti-SiO ₂	1150	125	47	30	18	11	4	-	-			
Sn-Ti-SiO ₂ *	1150	152	66	37	19	6	0	-	-			

*Note: Surfaces of oxide materials are polished. In systems indicated by *) the surface is rough with a microirregularities height of about 5 microns.

TABLE 3. The work of adhesion in titanium containing melts on high melting oxides at 1150°C, erg/cm².

System	Content Ti, % (at.)										
	0	1	2	3	4	6	8	10			
Au-Ti-Al ₂ O ₃	308	909	1100	1272	1366	1494	1547	1582			
Au-Ti-Ti ₂ O ₃	688	1000	1291	1480	1491	1590	1565	-			
Cu-Ti-MgO	422	1152	1894	3314	2317	2432	-	-			
Cu-Ti-Al ₂ O ₃	461	1331	2100	2265	2369	2470	2522	-			
Cu-Ti-SiO ₂	474	1503	2185	2265	2330	2422	-	-			
Cu-Ti-Ti ₂ O ₃	739	1280	1861	2184	2365	2475	2517	-			
Cu-Ti-TiO _{1.14}	1458	1611	1759	1864	1967	2136	2260	-			
Cu-Ti-TiO _{0.86}	1651	1792	1894	2020	2125	2265	2381	-			
Ni-Ti-Al ₂ O ₃ *	955	1100	1220	1320	1400	1525	1625	1775			
Sn-Ti-Al ₂ O ₃	185	697	770	799	810	831	-	-			
Sn-Ti-SiO ₂	198	782	867	903	921	928	-	-			

*Note: Surfaces of oxide materials are polished.

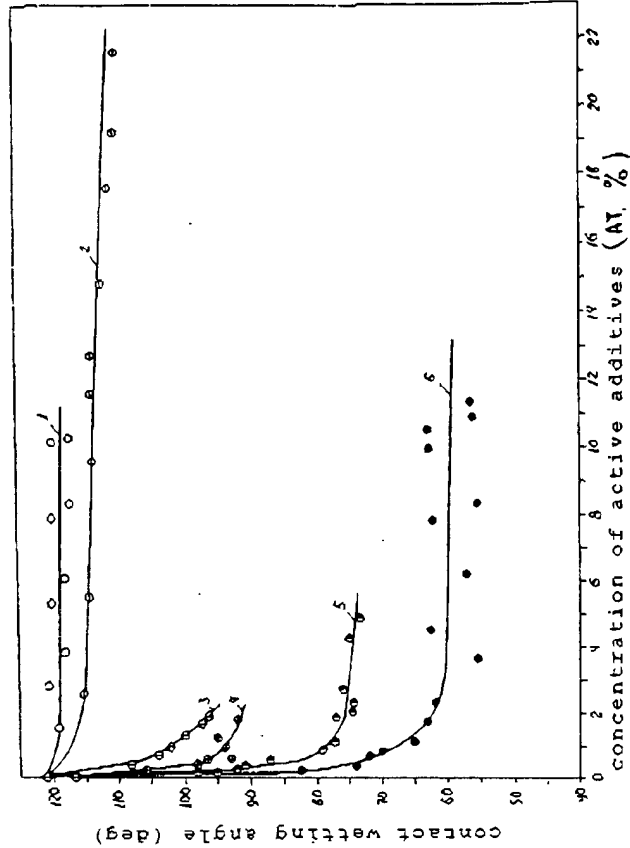


Fig. 11. Wettability of monocrystal aluminum oxide (plane 0001) by gallium-chromium (1,2), gallium-vanadium (3,4) and gallium-titanium (5,6) melts at 900°C (1,3,5) and 1050°C (3,4,6).

liquid phase. This has been established by direct measurements with a local micro-X-ray spectroscopic analysis. X-ray spectroscopic and microscopic studies have found oxide phases of TiO or Ti₂O₃ in the contact zone [102,103].

It is interesting to note that in systems or under conditions when TiO oxide occurs at the boundary having "metal-like" properties (high electrical conductivity, metallic lustre, metallicity of interatomic bond), the wettability is higher than in the systems where the oxide Ti₂O₃ is formed. The latter oxide has interatomic bonds of a substantially ionic nature [104]. The data are presented in Table 4. The wettability of TiO by metals is much greater than that of Ti₂O₃. From Table 2 and 3 it follows that the contact angle of liquid copper is 72° for TiO_{0.86} and 113° for Ti₂O₃.

TABLE 4. The work of adhesion and phase composition of transition layers in titanium containing melts (2%(at.)Ti) or high melting oxides.

Group	System	Temperature °C	Work of adhesion erg/cm ²	Transition layer	Method of transi- tion layer identification
I	Al-Ti-Al ₂ O ₃	1150	1100	Ti ₂ O ₃	X-ray
	Ti-Ti-Al ₂ O ₃	1500	1220	Ti ₂ O ₃	"-
	Li-Mo-Ti-Al ₂ O ₃	1500	1500	Ti ₂ O ₃	"-
	Sn-Ti-SiO ₂	1150	867	Ti ₂ O ₃	Visual*
II	Cu-Ti-Al ₂ O ₃	1150	2100	TiO	X-ray
	Cu-Ti-MgO	1150	1894	TiO	Visual
	Cu-Ti-SiO ₂	1150	2185	TiO	"-

*Note: Titanium oxides Ti₂O₃ and TiO differ sharply in color. While using transparent solid phase materials (quartz glass, sapphire), the intermediate layer color is observed visually and can serve the indication of preferential formation of this or that titanium oxide.

Where competitive interaction exists between the liquid metal and the metal which forms the oxide, oxygen can transfer into the liquid phase metal, either forming an intermediate oxide layer or dissolving in the metal. In either case, a contact between the metal-oxygen alloy and the oxide surface is taking place. To understand the mechanism of cohesion between the liquid metal and the solid oxide, it is important to study contact processes in the system solid oxide - liquid metal melt, containing oxygen. Such systems can be considered as a type of model of intermediate states of metal-oxide interactions.

Interesting peculiarities of metal-oxygen alloys are mentioned in the literature. It has been found that on adding oxygen to a liquid-metal melt of iron [64,68,87] or silver [55] the contact angle sharply decreases for the wetting of the oxide surface by the metal. For iron containing 0.04% of oxygen the contact angle on aluminum oxide was 109° against 147° for the pure metal; for silver which wets oxides CdO, ZnO, MgO the angle of contact decreased from

110 to 140° for pure silver to 90° for silver saturated by oxygen from air.

Similar phenomena were observed earlier in steelmaking processes [88,89,90]. Metallurgists noted that "killed" steel wets the bottom worse than "nonkilled" steel. This was confirmed by observations of improvement of the metal-ceramic bond for the Al₂O₃-Cr system [91] as well as the Mn-Al₂O₃ and Mn-Al₂O₃ system [92] after introducing atmospheric oxygen into the metal.

Oxygen effects on surface and contact properties of metals was studied in detail in [93-97,107-109]. In these works, the surface tensions of melts of such systems as Fe-O, Ni-O, Cu-O, Ag-Cu-O have been studied together with their wetting characteristics on aluminum and manganese oxides. The results of some of these studies are presented in Figures 12-15. Oxygen causes an abrupt decrease of the surface tension of the melt and improvement of ability of the melt to wet the oxide surface. The contact angle for copper on aluminum oxide at 1100°C is equal to ~130° but drops to ~60° with an oxygen content of 1-2% in copper. Copper-oxygen melts (alloys of copper and copper oxide) intensively wet corundum monocrystal and manganese oxide, as well as some other ceramic oxide phases [108, 109]. As the oxygen content increases, the wettability and adhesion of iron to monocrystal aluminum oxide (sapphire) grows [107]. Surface and interphase activity (relative to oxide phases) of oxy-

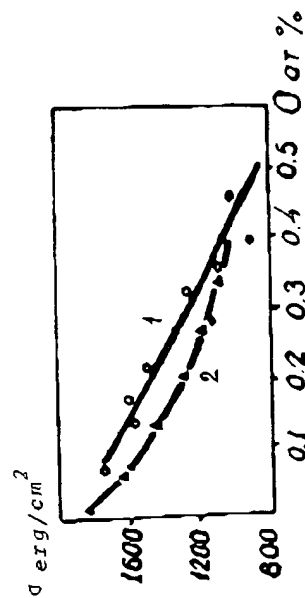


Fig. 12. Surface tension of alloys Ni-O (1500°C, curve 1), Fe-O (1550°C, curve 2).

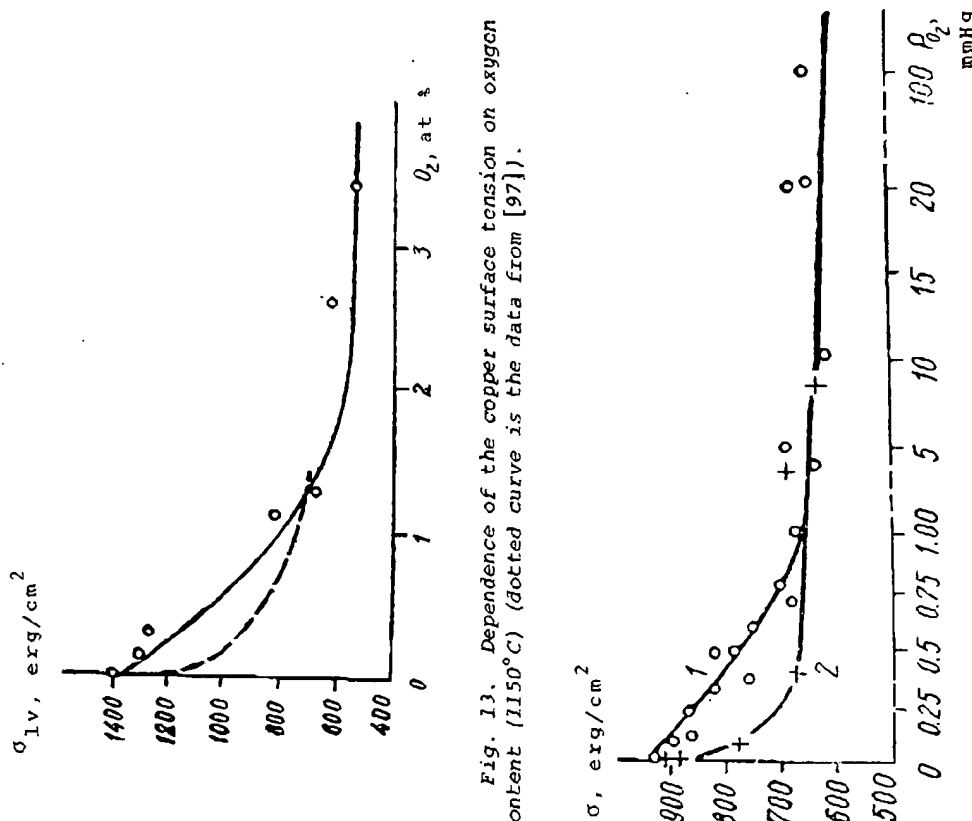


Fig. 13. Dependence of the copper surface tension on oxygen content (1150°C) (dotted curve is the data from [97]).

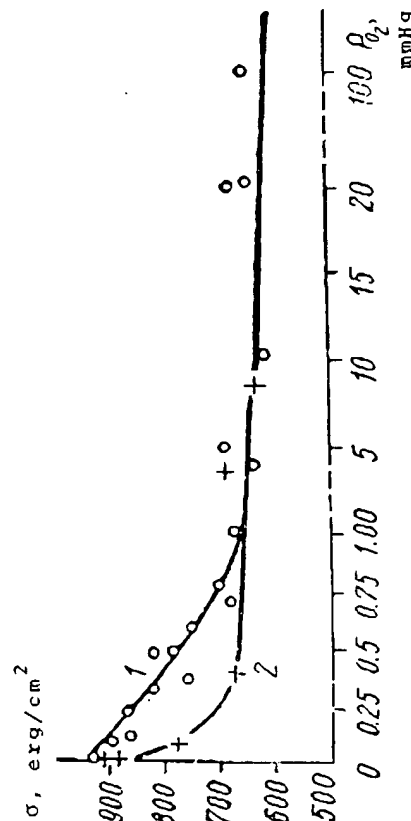


Fig. 14. Oxygen pressure in the gas phase affecting the surface tension of the liquid silver (1) and the alloy Ag-58 Cu (2) (1000°C).

gen becomes apparent for alloys Pb-O [69]: oxygen facilitates better adhesion of gold to a quartz surface [58], as well as that of gallium to both quartz and sapphire surfaces [106]. Absence of oxygen improves adhesion to the glass surface of spray-coated films of

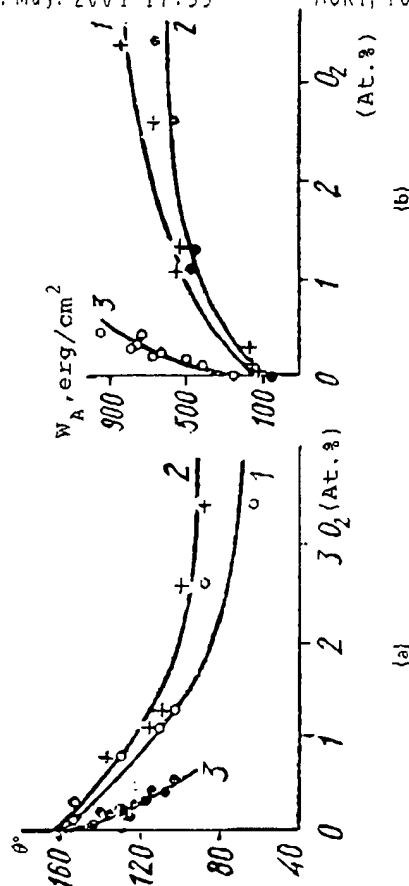


Fig. 15. (a) The effect of oxygen dissolved in the liquid metal on wettability of solid oxides 1-the system copper (oxygen)-aluminum oxide; 2-the system copper (oxygen)-magnesium oxide; 3-the system nickel (oxygen)-aluminum oxide. (b) Adhesion work in the systems: 1-copper (oxygen)-aluminum oxide (1150°C); 2-copper (oxygen)-magnesium oxide (1150°C); 3-nickel (oxygen)-aluminum oxide (1500°C).

lead, nickel, iron, molybdenum, gold, copper, zinc, and other metals [29]. It remains to be shown what the reasons are for the surface metal-gas interface and interphasic metal-oxide interphase activity of oxygen.

In accordance with the statistical molecular theory of adsorption (see [98] for example), the surface properties of binary solutions, the surface activity of the components and even extreme adsorption can be described by means of the value:

$$F = \exp(\Delta/RT)$$

where

$$\Delta = -\bar{E}_{q1}^w - \bar{E}_{q1} + \bar{E}_{q2}^w - \bar{E}_{q2}$$

\bar{E}_{q1} and \bar{E}_{q2} are the potential energies of molecules of the first and the second components, \bar{E}_{q1}^w and \bar{E}_{q2}^w the energies of these components in the surface layer and in the bulk solution, i.e. Δ is

the difference of the transition work from the bulk volume into the surface of the first and the second component. Δ is included in all the basic formulae and determines the value and the sign of the adsorption of each component. In particular, positive adsorption of the first component can be observed at $F > 1$ and $\Delta < 0$, i.e., the element would be surface-active if its work of transition into the solution surface layer is less than that of another component.

By means of simple calculation for dilute oxygen solutions (component 1) in a metal (component 2), the values of Δ can be expressed approximately through bond energies between the nearest atoms in solution.

For the liquid-gas interface

$$\Delta_{\text{liq.vap.}} = \frac{1}{2} \left(z_v - z_s \right) \left(u_{22} - u_{12} \right) + \left(z_s c_1^s - z_v c_1 \right) \left(\frac{u_{11} + u_{22}}{2} - u_{12} \right) \quad (17)$$

For liquid-solid interfaces

$$\Delta_{\text{liq.sol.}} = \Delta_{\text{liq.vap.}} + z_s' (u_{1s} - u_{2s}) \quad (18)$$

Here u_{12}, u_{11}, u_{22} are bond energies between adjacent atoms 1-2, 1-1, 2-2; u_{1s} and u_{2s} are the respective bond energies of metal and oxygen with surface atoms of the solid phase; z_v and z_s are the coordination numbers inside and at the liquid-gas surface; z_s' is the number of bonds each metal atom forms with its neighbors at the solid oxide surface; c_1^s, c_1 are the first component concentrations in the surface layer and in the bulk solution.

In considering the freshly formed surface of the diluted solution (the initial stage of the adsorption process), i.e., $c_1^s \approx c_1 \gg 1$, we neglect the second term in formula (17). With a positive value of Δ , the surface activity of component 1 (its tendency to adsorb at the surface) would be observed at $u_{22} > u_{12}$, i.e. when interactions between solvent atoms would be stronger than those between solvent and solute atoms. Subsequently, as the surface is saturated by the component 1 with c_1^s growth, the second term in

formula (17) begins to play a role, i.e. in addition to the condition $u_{22} > u_{12}$, a sufficiently high bond energy between component 1 atoms is essential for a high adsorption value. Component adsorption at the liquid-solid interface is determined by combined action of the two factors: displacement of the component from the bulk melt (the tendency of the component 1 atoms to be surrounded by the least number of neighboring atoms of component 2) and the affinity of component 1 atoms for solid body atoms.

One can assume that oxygen in the metal melt (Fe, Ni, Cu and so on) exists essentially in the form of O^{-2} ions or to be more exact in the form of an $Me^{+2}-O^{-2}$ complex, spatial separation of the oxygen and the metal ion being impossible. The oxygen-metal bond in the solution is partially ionic and partially covalent (metallic) with the ionic character prevailing. The ionic bond character increases with growing difference of the electronegativities of oxygen and the metal in which it is dissolved.

There arises a question about the strength of such a complex bond with the matrix metal. This bond obviously involves a positive metal ion. Localization (partial or complete) of this ion's external electrons on the oxygen ion should weaken the intensity of the metallic bond with the remainder of the metal atoms, i.e. a bond between the metallic ion of the metal-oxygen complex and another metal atom should be weaker than that of metallic atoms with each other. Thus the bond energy $U_{\text{compl.-Me}} < U_{\text{Me-Me}}$ which is in accordance with (17) and is the condition of metal-oxygen complex surface activity, i.e. determines adsorption of the oxygen dissolved in the liquid metal. It is also necessary to find out in which way the oxygen surface activity is affected by the strength of its binding with the metal in which oxygen is dissolved, i.e. the strength of its binding in the complex. Usually as the difference of metal and oxygen electronegativities increases, the ionic character of the bond in the oxide increases, the metallic (covalent) contribution to the bond decreases and the bond strength grows. In the same way the metallic properties of the oxide diminish (in particular this refers to intrinsic electrical conductivity).

The ionicity growth of the ionic character of the metal-oxygen bond in the complex will result in a greater localization of metal electrons near the oxygen ion, i.e. to their not taking part in the metallic bonding of the complex metal ion with the rest of the metal atoms, i.e. to a greater shift of oxygen surface activity $U_{\text{Me-Me}}^{\text{compl.-Me}}$ to higher values. With a very strong bond between the metal and oxygen, the bond energy $U_{\text{compl.-Me}}$ can drop to such an extent that the solubility of such complexes (and eventually that of oxygen in the liquid metal would drop sharply; second phase (metal oxide) formation will take place.

Thus as the bond between metal and oxygen becomes stronger the surface activity of the latter should grow when it is dissolved in metal. With very high values of the metal-oxygen bond energy, the surface activity of oxygen can be insignificant due to very low solubility of oxygen in the liquid metal. The value of the heat of oxide formation can be the criterion of the strength of the metal-oxygen bond in the complex dissolved in the metal.

For metal-oxygen systems, the bond energy of the metallic positive ion of the complex $\text{Me}^{+2}\text{-O}^{-2}$ and the oxide surface formed by negatively charged oxygen ions would be larger than that of the neutral metal ion and oxygen ion of the surface oxide, i.e. $U_{1s} > U_{2s}$ due to the substantial coulombic energy of interaction in the first case. Consequently in systems where there is an oxygen solution in the liquid metal at the boundary with the solid oxide, both factors in formula (18) act in the same direction intensifying oxygen adsorption (complex $\text{Me}^{+2}\text{-O}^{-2}$ adsorption, to be more exact) at the interface.

The theoretical considerations developed above are designed to meet the following requirements: (1) oxygen dissolved in the liquid metal should be surface active at the liquid-gas interface. Oxygen surface activity at the interface should grow with the strength of metal-oxygen bond (thermal effect of oxide formation); (2) oxygen should be active at the metal melt-oxide interface; it is to be noted that interfacial activity and adsorption of oxygen

at the interface should be higher than the corresponding value at the metal-vacuum boundary.

The requirement of oxygen surface activity is confirmed experimentally as has been demonstrated above. Oxygen dissolved in liquid, copper, nickel and iron sharply lowers the surface tension of these metals. A comparison of oxygen surface activity in these systems is presented in Table 5.

The surface activity of oxygen in the silver-oxygen system as a function of concentration is not known; the only known value is that of $\frac{d\sigma}{dp}/p \rightarrow 0$ where p is the oxygen partial pressure [95]. Nevertheless from Fig. 14, where $\sigma - p$ isotherms for the system silver-oxygen and silver-copper alloy-oxygen are shown it may be seen that the oxygen surface activity in the latter is much higher. Hence one can state that

$$\frac{d\sigma}{dc} \frac{Ag+O}{c} + 0 < \frac{d\sigma}{dc} \frac{Cu+O}{c} / c \rightarrow 0$$

With allowance for this, it follows from Table 5 that with increase of heat of oxygen formation and of the strength of the metal-oxygen bond, oxygen surface activity grows.

These data can be explained on the basis of electron localization. The degree of electron localization on the oxygen ion in the complex $\text{Me}^{+2}\text{-O}^{-2}$ depends on the electron affinity of the metal

TABLE 5. The surface activity of oxygen in the metal alloy in comparison with heat of metal oxide formation and the affinity of the electron for the bivalent metal ion (the second ionization potential).

System	$\Delta H_{298}^{\circ} \text{Me-O}$ kcal/mole	$I, \text{ eV}$ (the second ionization potential of metal)	$\frac{d\sigma}{dc} \frac{1}{c \rightarrow 0}$ dyne/cm \cdot at%
Ag-O	-7.3	21.48	-
Cu-O	-41.0	20.29	720 [94]
Ni-O	-58.4	18.15	2400 [93]
Fe-O	-63.7	16.18	3000-3500 [87]

ion, in this case on the second ionization potential of metal. A low ionization potential means a greater degree of electron localization on oxygen ion (i.e. an increased ionic character for the complex bond. There will also be a decreased participation of electrons in the metallic bonds of the metal ion with the rest of metal atoms. Such a complex is less strongly bonded with other metal atoms and according to (17) is more surface active. A high metallic ionization potential indicates a decreased localization of electrons on the oxygen ion, a greater degree of covalent bonding in the $\text{Me}^{+2}-\text{O}^{2-}$ complex (approaching that of the metallic bond), a stronger bond between the complex with other metal atoms and reduced surface activity of oxygen. The values of the second ionization potentials of iron, nickel, copper and silver are given in Table 5. In accordance with the above statements, the surface activity of oxygen in the metal grows as the ionization potential decrease.

Experiments have demonstrated considerable interfacial activity of oxygen at the metal-oxide interface and increased oxide surface wettability by oxygen-containing metal melts (Fig. 15). Note: The surface and interfacial tension decrease was calculated for $C = 3 \text{ at.}\%$ oxygen for the system copper-oxygen and $C = 0.5 \text{ at.}\%$ oxygen for the system nickel-oxygen; Γ is the value of adsorption:

$$G = \frac{\partial G}{\partial C} C + 0.$$

As it is seen from Table 6 interfacial tension decrease at the metal-oxide interface under the influence of oxygen addition, is much stronger than that at the metal-gas interface. The calculated values of adsorption at the solid body-liquid interface are higher under all oxygen concentrations than that at the liquid-gas interface. This agrees with the theoretical concepts being considered.

Great amounts of oxygen localized near the solid-liquid interface (as compared to that at the liquid-gas interface) are indicative of the fact that oxygen ions are bound by additional adhesion bonding to the oxide surface. However, taking into account the

TABLE 6. A comparison of the metal-gas and metal-oxide interfacial activity of oxygen

System	The liquid-gas interface	The liquid-solid body interface
	$G_{lv} = \sigma_{lv} - \sigma_{lv}^c$ dyne/cm	$G_{sl} = \sigma_{sl} - \sigma_{sl}^c$ dyne/cm
	$\Gamma_{lv}^{max} \times 10^{10}$ mole/cm ²	$\Gamma_{sl}^{max} \times 10^{10}$ mole/cm ²
	dyne/cm·At%	dyne/cm·At%
Cu-O-Al ₂ O ₃	720	800
Cu-O-MgO	720	800
Ni-O-Al ₂ O ₃	2400	1100
	43	43
	930	1200
	1260	1400
	56	52

fact that the oxide surface consists of negatively charged oxygen ions which shield the metal ions, it is difficult to assume that direct adsorption of oxygen anions takes place. It should be considered that at the oxide surface positively charged ions of the liquid metal are adsorbed (one can speak about adsorption of complexes, $Me^{+2}O^{-2}$ oriented and located in such a way that the metal ion faces the oxide surface and is situated near the oxygen ion of the oxide). Metal ions are bound by strong ionic bonding with the solid oxide anions, thus completing its lattice; oxygen ions from the liquid metal are attached in the positively charged nodes, i.e., a layer of liquid phase metal-oxide is formed at the interface. Such an interfacial structure is confirmed by metal diffusion in the liquid phase observed in some systems by means of microscopic study. Such diffusion takes place in the lattice along the boundaries of the solid oxide grains (copper [96] and iron [97] in aluminium oxide).

The energy of interaction between the oxidized metal and the oxide surface on the basis stated above can be estimated in the following way. Since metal ions of the liquid phase are adsorbed on oxygen ions of the oxide and oxygen of the liquid phase evidently occupies positions between metal ions or close to them, the bond energy of an oxygen containing liquid metal-solid oxide systems may be presented as the energy of interaction between the oxide layer of the liquid metal and a semi-infinite lattice of the solid oxide. This energy is determined by summation of terms of the type $\frac{r_{ik}}{2i \cdot 2k \cdot e^2}$ - coulomb potentials of interaction between the i -th ion of the liquid phase oxide and the k -th ion of the solid oxide, i.e. this is the analog of Madelung bond energy in ionic crystals. It is possible to calculate the exact sum and to allow for the bond components (repulsive energy, energy of van der Waals forces, etc.) as is done in the theory of ionic crystals. However taking into account the approximate character of computation one can make use of the procedure given below in this particular case.

Let us substitute for liquid phase metal oxide layer, which has

a finite thickness (two-three planes of atoms), an infinite oxide layer. Bearing in mind that the main contribution to the bond energy is that of the first layers of atoms of the liquid metal oxide, we shall consider that the bond energy of the oxidized liquid metal with that of the solid oxide to be approximately equal to the bond energy of a semi-infinite crystal of the solid oxide with a semi-infinite crystal of the liquid phase metal oxide, i.e., to be equal to the work of separating those halves of the crystal along the plane of contact. In the case when the lattice parameters of both oxides and the ionic valencies of both metals (metal of the solid phase oxide and the liquid metal) are similar, the given energy can be taken as double the surface energy of the corresponding ionic crystal. The latter has been correctly calculated in many works [85,99]. For lattices of the NaCl-type (oxidized liquid copper or nickel on magnesium oxide), the surface energy of the face (100) is $0.116 (ze)^2/d^3$, according to [85] where d is the cube root length of the elementary cell. Assuming $a = 4.26 \text{ \AA}$ for copper oxide (close to the value of a for magnesium oxide equal to 4.21 \AA) and $z = 2$ for the adhesion work we obtain $W_a = 2 \cdot \sigma = 2.0$, $0.116 (ze)^2/d^3 = 2.5 \cdot 10^3 \text{ erg/cm}^2$, i.e. the order of magnitude of this energy is 10^3 erg/cm^2 .

Experimental values of the adhesion work for the system $Ni(O)-Al_2O_3$ at an oxygen content in nickel of 0.475 at.%, are approximately 950 erg/cm^2 . As is seen from the plot (Fig. 15) the value of the adhesion work should increase slightly with increasing oxygen content. For the system $Cu(O)-MgO$, the adhesion work was 630, while for $Cu(O)-Al_2O_3$ it was 785 erg/cm^2 .

Though it was not our aim to obtain numerical values of the adhesion work, the calculations carried out allow us to conclude that the coulombic energy of interaction of the dissolved liquid phase metal and oxygen ions with the solid oxide surface is high enough to explain the adhesion work of the oxidized metal and the solid oxide experimentally observed.

Summarizing the mechanism of action of oxygen dissolved in the

liquid metal on the metal adhesion properties the following is to be pointed out:

(a) Neutral atoms at the liquid metal surface cannot be bound by strong chemical bonds with the oxide surface formed by negatively charged ions of oxygen. If it is taken into account that the metal surface is also electrically negative (a layer of electron gas penetrating beyond the metal lattice) then one should suppose that there are repulsive forces acting between the metal and the oxide.

(b) A metal-oxide bond is formed when the atoms of the metal get rid of their valence electrons and give them up to atoms of oxide oxygen. Positive metal ions are then bound by strong ionic bonds to the oxygen ions at the oxide surface.

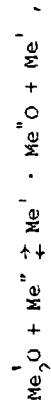
Thus, ions of oxygen dissolved in the liquid metal are to be treated as the sites of electron extraction (in the liquid metal). The role of oxygen in this case is evidently not specific; it can be substituted by any other metalloid ion (sulphur, halogens, complex anions of the SO_4^{2-} type and many others) soluble in the liquid metal and having sufficient affinity for electrons. Thus, sulphur acts like oxygen in the system $Fe-Al_2O_3$ [64,100]. Selenium and tellurium in $Pb-UO_2$ [69] and chlorine in $Bi-UO_2$ [70] behave in a similar way. The intensity of the metalloid effect on the interfacial tension decrease is determined not only by the factors listed above but also by the relationship of the anionic dimensions (or, to be more exact, of the magnitude of the lattice parameters of the intermediate ionic structure being formed) and those of the solid phase oxide. It should be emphasized that it is necessary for metal atoms to get rid of their valence electrons for bond formation between the metal and the oxide surface to take place. From this point of view, the mechanism of bond (adhesion) between the liquid metal and the solid oxide can be described in the following way:

At absolute zero temperature an ideal metaloxide lattice would

have the ionic component of the bond between metal and oxygen ions having the structure of inert gases atoms (closed electron shells). As has been mentioned above, under these conditions the neutral metal atom from the liquid phase cannot form any strong chemical bond with the oxide.

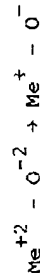
As temperature is increased, thermal motion disturbances in crystal structure are taking place, in particular electrons can pass from the oxygen ion (O^{2-}) to the metal ion. An oxygen ion O^- is formed with a local dissociation of the oxide taking place between an atom of oxygen and an atom of the metal. In some oxides electron holes are formed in the electron levels of metal ions ($Ni^{+2} \rightarrow Ni^{+3}$ for instance). At each temperature, a certain equilibrium number of O^- ions and oxygen atoms is established. Equilibrium is also established between the number of dissociated ions and of oxygen atoms inside and at the surface of the crystal.

O^- ions or oxygen atoms formed at the crystal surface have a positive valency. The metal atom in contact with the oxide on filling the vacant site by its valence electrons (getting rid of its valence electrons) can be bound by strong ionic bonds with the oxide surface thus completing its lattice. For monovalent solid oxide metal and liquid metal the reaction which is taking place can be written as follows:



where Me' is the solid oxide metal; Me'' is the metal reacting with the oxide (in this case with the site where metal valence electrons are localized is the oxygen atom (ion) of the oxide lattice).

The subsequent development of the bond of the oxygen ion with the liquid phase metal atom is somewhat different. If there is a partial dissociation of the bond $Me-O$ in the solid oxide, for example



then the oxygen ion remaining at the surface is saturated by the

valence electron of the liquid metal atom ($O^- \rightarrow O^{-2}$) and will form the binding bridge between the liquid metal and the oxide.

With complete bond dissociation in the solid oxide the oxygen atom is released, and can pass into the liquid metal, localizing valence electrons of the metal and reforming an O^{-2} ion. A positively charged metal ion is adsorbed at the neighboring oxygen ion of the oxide while the released oxygen ion already adsorbed on the liquid phase side) is fixed on the metal ion. If in the liquid phase metal oxygen is sufficiently soluble, then some of oxygen ions will pass into the metal melt with some locating at the metal-gas interface. Here the role of oxygen is the same as in the case of metal-oxygen systems considered above. If oxygen solubility in the liquid metal is low, then oxygen released due to the metal-oxide reaction and saturated again with metal electrons to reform the O^{+2} state remains localized near the interface on the liquid metal side.

In all of the above cases, a layer of the corresponding metal oxide, completing the lattice of the solid phase oxide, is formed on the liquid metal phase side of the interphase. However when metal ions M^{+2} are available beforehand (e.g. when metal-oxygen solutions readily form) the metal-oxide bond is easily formed and the oxidized metal wets the surface of the ionic compound. In the case of pure metals and oxides, additional energy is needed for oxide dissociation. That is why a liquid metal does not usually wet an oxide with strong interatomic bonding.

A numerical estimation of the bond energy between metal and oxide (the adhesion work) can be carried out using expressions (9)-(11). For this purpose it is necessary to calculate the dispersive energy interaction between the metal and the oxide and the energy of the chemical reaction taking place at the interface, when the reaction takes place according to the equation:



where Me'' and Me' are substances Me'' and $Me'O$ (moles/unit in-

terface area) are equal to n' and n'' respectively, then the concentration of each of the four substances can be expressed through the degree of reaction transformation α :

$$[Me''] = \frac{n'' - \alpha}{n'' + n''}; \quad [Me'O] = \frac{n' - \alpha}{n' + n''}; \quad [Me'] = [Me''O] = \frac{\alpha}{n' + n''}$$

The equation of the reaction isotherm can be written as

$$\frac{dZ}{d\alpha} = RT \ln \frac{\alpha}{(n' - \alpha)(n'' - \alpha)} - RT \ln \frac{\alpha_0}{(n' - \alpha_0)(n'' - \alpha_0)} \quad (20)$$

where α_0 is the equilibrium degree of the reaction transformation. The adhesion work is calculated by integrating this expression

$$W_a = \int_0^{\alpha_0} \frac{dZ}{d\alpha} d\alpha = -RT \left[n' \ln \left(1 - \frac{\alpha_0}{n'} \right) + n'' \ln \left(1 - \frac{\alpha_0}{n''} \right) \right] \quad (21)$$

α_0 can be found from the expression for the equilibrium constant and from the isobaric potential change in the course of this reaction

$$\Delta Z = \Delta Z'' - \Delta Z' = -RT \ln \frac{\alpha_0^2}{(n' - \alpha_0)(n'' - \alpha_0)} \quad (22)$$

$\Delta Z''$ and $\Delta Z'$ are changes of isobaric potentials on oxidizing the Me'' and Me' metals, respectively.

The dispersion energy of the bond between the metal and the oxide W_{AB} can be estimated from relations given in chapter 1 by allowing for the interactions of the nearest atoms disposed in the first contact atomic planes of the metal and the oxide.

The distance R in formula (11) for the bond energy was assumed equal to the metal atom radius (a half of the least distance between the metal atoms in its closest packing structure) added to the radius of oxygen ion $R_{O^{-2}} = 1.4 \text{ \AA}$. According to Pauling, the polarizability of the oxygen ion is 3.08 \AA^3 ; in agreement with reference [29], the ionization potential of the oxygen ion (O^{-2}) is

$89 \cdot 10^{-12}$ erg. For metal-oxide systems one can take into account only bonds of metal atoms with oxygen ions. Any additional energy of the dispersion bond of the metal-metallic oxide ion junction due to the low polarizability of the latter and its high ionization potential constitutes only a small correction (about several per cent). It is, however, necessary to take values of the third and the fourth ionization potential for bi- and trivalent metallic ions respectively.

The contact angle was calculated by the formula $\cos \theta = \frac{W}{\sigma_{lv}} - 1$. For sufficiently intensive interaction of the contact pair components, the liquid metal is saturated by the products of reaction with the oxide (oxygen in particular). For the system Ni-NiO, the surface tension of nickel is assumed equal to 1000 dyne/cm; the surface tension of titanium and zirconium in contact with oxides is unknown and the angle of contact for those systems has not been determined. The calculation data is summarized in Table 7 from which it is seen, at sufficiently large negative values of Δz , that the calculated chemical part of the adhesion work is comparable with the experimental one (the same order of magnitude). At positive Δz values the calculated chemical part of the bond energy is small compared to the value of the energy due to van der Waals interaction.

Up to now the discussion has concerned the wettability of metal oxides by metals. It seems possible to now generalize features of contact interaction between the metal and the oxide and to extend them to the case of any ionic compound of metal with non-metal (or complex anion) whose crystals consist of cations and anions (sulphides, various high-melting salts--sulphates, phosphates, halogens, and so on).

The large radius of the anion and its high polarizability are characteristics for such compounds, i.e. their surface is formed by negatively charged ions due to the circumstances considered above. The most important interaction of the liquid metal and the surface is that of the liquid metal and the crystal anion.

TABLE 7. The work of adhesion and wettability in metal oxide systems

System	T°K	Δz kcal/g-atom of oxygen	Radius of metal atom r_m	Polarizability α_m 10^{-24} cm ³	W_a (chem) erg/cm ²	W_a (VDW) erg/cm ²	W_a (total) erg/cm ²	θ°
Au-Al ₂ O ₃	1370	98	1.44	1.27	0	240	240	142
Ag-Al ₂ O ₃	1270	100	1.44	1.86	0	380	380	125
Fe-BeO	1820	64	1.28	1.79	.15	490	490	137
Si-MgO	1450	20	1.34	1.63	40	320	360	120
Ni-NiO	1650	0	1.24	1.88	500	480	980	1470
Sn-NiO	1275	-7	1.58	2.02	715	190	905	955
Ti-MgO	2000	-6	1.45	2.32	920	350	1270	2000-2500
Zr-MgO	2100	-13	1.58	2.27	1320	220	1540	2500
								-

The ionic crystal wettability by the liquid metal will be greater the greater the affinity of the liquid metal for the non-metal (complex anion) and the weaker the bond of non-metal with the solid compound metal, i.e., wettability will be directly connected with the value

$$\Delta Z = \Delta Z' - \Delta Z''$$

where $\Delta Z'$ and $\Delta Z''$ are the changes of thermodynamic potential on forming compounds with the metalloid of the liquid metal phase and with the metal of the ionic crystal of the solid phase. In this case the addition of a metalloid to the liquid metal having sufficient electron affinity to pull electrons away from metal atoms and transform them into positive ions will promote ionic crystal formation and wettability by the metal melt.

There is practically no experimental data on the wettability of various ionic compounds by liquid metals. The author has studied adhesion properties of liquid copper on the high melting salt CaF_2 . The tests were carried out at 1320°C in helium. At this temperature, the thermodynamic potential of CaF_2 formation is 115, of CuF_2 45 kcal/g. atom of fluorine. Thus

$$\Delta Z = \Delta Z_{\text{CuF}_2} - \Delta Z_{\text{CaF}_2} = +70 \text{ kcal}/2 \cdot \text{atom F}$$

i.e. ΔZ has a large positive value. Based on the curve in Fig. 11 for the system Cu-CaF_2 one should expect nonwettability and a small work of adhesion. Introduction of the "strong" anion (that of oxygen, for example) into copper should increase the degree of wettability.

The experimental study results for the system Cu-CaF_2 are presented in the table:

Solid phase	Liquid phase	θ°	$W_a \text{ erg/cm}^2$
CaF_2	Cu	140	300
	$\text{Cu}+1, 5\% \text{ O}_2$	80	620

Pure copper forms a large angle of contact at the surface of

CaF_2 . Addition of oxygen sharply increases the wettability of the solid surface and the adhesion of the alloy. These data are in agreement with the generalizations previously stated.

B. The Wettability of Covalent Solids by Metals

Covalent high-melting solids (elementary substances and compounds) among which such technically important compounds as diamond, graphite, silicon carbide and nitride, boron nitride (hexagonal and cubic), and boron carbide (B_4C) will be considered here. They are characterized like ionic compounds by closed stable electron configurations of atoms with high strength interatomic bonds. The equilibrium part of the adhesion work $W_a(\text{eq.})$ arising through mutual saturation of free valences is negligible for the interaction of such bodies with metals. Interaction and high adhesion energy (and wettability) are possible only at the expense of bond dissociation in the solid phase and chemical reaction between the metal and the solid body (contribution of $W_a(\text{non-eq.})$). The metal should possess high chemical affinity to any kind of solid phase atoms.

The data and characteristics of these covalent solid bodies wetting by metals are considered below.

1. Adhesion to, and wettability of, diamond and graphite by metals. From the above discussion it can be assumed that those elements having a high wettability will enter into substantially intensive chemical interaction with carbon, i.e. they will form carbides, dissolve carbon and diffuse inside the solid phase.

The interaction of carbon with metals will depend significantly on the properties of the latter and different types of bonds between atoms of metal and carbon can be established. The electronic structure of carbon atoms ($1s^2 2s^2 2p^2$, there are four valence electrons) is such that carbon can be either a donor or an acceptor of electrons depending on the conditions. Metalloid properties of carbon atoms usually manifest themselves in its interpretation with strong electronegative elements, i.e. with the elements on the left-hand side of the periodic table: alkali and alkaline-earth

metals having low ionization potential. These elements form salt like compounds with carbon (carbides) with a substantial degree of ionic bonding between the atoms of Me-C. Thus alkali metals intruded into the graphite lattice in the space between the layers are positively ionized forming polycarbides of the type MeC_8 , MeC_{16} , for example [114,140,145,147].

Alkaline-earth metals form also compounds with carbon of the salt like carbide type (MeC_2) where the bonding between the metal and carbon atoms is mainly ionic.

In the interaction of carbon with transition metals (metals with an unfilled d-electron shell) carbon displays its metallic donor properties giving up a part of its outer electrons to the d-band of metal. This situation, formulated first by Ubbelode [148] for hydrides of transition metals, was developed in works by Umansky, Samsonov [141,142] and Kissling [150] for the interaction of carbon and transition metal in carbide metals. Several factors favor the transfer of valence electrons from the carbon atoms to the d-band of the transition metal alloy with positive ionization of the carbon on binding. These factors are the metallic character of carbide phases (phases of intrusion): the small size of carbon ions and their high mobility of diffusion in carbides (much higher than that of oxygen or sulphur anions in oxides and sulphides); the relationship between the heat of formation of the carbide and the occupancy of d-bands of the metal; the substantial difference of lattice parameters of titanium and vanadium carbide experimentally observed and that assumed from calculation of ionic bonding in Ti^+-C^- and V^+-C^- .

According to Bruer [151] the fact that carbon is the donor of electrons, supplying them to d-band of the metal, can be confirmed by a shift of the stability maximum (heat automatization) of solid phases which for transition metals is localized in groups V-VI of the periodic system (formation of stable electron structures d^5), and for carbides in the group IV.

In [152,153] using electron transfer data, the charge of carbon

dissolved in transition metals has been determined. The data obtained indicate that carbon is the cation whose value of charge in different alloys is:

Metal	Ti	Ta	W	Fe	Co	Ni
Value of carbon charge	+4	+2.8	+0.6	+3.8	+2.6	+1.8

The degree of carbon ionization is related to the degree of filling of transition metal levels.

The author's investigations allowed him to conclude that carbon should be positively ionized during its dissolution in nickel melts [10]. On the other hand, while some authors consider the ionic component to be the substantial part of the bond between carbide and transition metal in carbides, they ascribe the negative charge to the carbon. According to [143] this is confirmed by the decreasing lattice parameter in an isoelectron row of compounds (structures of the NaCl type): $\text{K}^+\text{F}^- + \text{Ca}^{+2}\text{O}^{2-} + \text{Sc}^{+3}\text{N}^{3-} + \text{Ti}^+\text{C}^-$, namely: 5.33, 4.80, 4.44, 4.31 Å with the growth of both the metal and the anion valency (fourfold negative ionization of carbon is assumed in TiC). Also, in [154] on the basis of an analysis of the electron density distribution in titanium carbide, the author made a conclusion that the carbon ion was negatively charged (about -1).

It should be noted that from this point of view many characteristic properties of carbide phases (their high electric conductivity, the mobility of carbon atoms and so on) prove difficult to treat. Particularly the role of nonoccupancy of the d-electron shell and its relationship with the interatomic adhesion strength for the carbon-metal junction is not clear.

Thus, preference should be given to the first interpretation and it is to be assumed that in the interaction of carbon with transition metals, bonds of metallic character are established and that the carbon atom is positively ionized.

Covalent bonds are usually formed with carbon when bonded to metallic elements with outer 2p or 3p electrons. Boron and silicon

are typical representatives of this group. These elements can still form stable carbides. However, when the main quantum number increases to $n \rightarrow 4$ then the strength of covalent bond p metal-carbon decreases so sharply that the given elements are already practically inert to carbon.

With regard to their interaction with carbon, metals with complete f -electron shells (lanthanoids and actinoids) should be separated into an individual group. Those elements form "saltlike covalent-metallic" carbides. Small values of the first ionization potentials of lanthanoids result in a substantial ionic contribution to the bonding of the metal with carbon. On the other hand, these metals have nonoccupied shells. As in a "d-transition" this should impart a certain metallic character to the bonding which takes place in such carbides. The latter carbides possess the most characteristic feature of metals, high electrical conductivity of the metallic type. Actinoids give still more "metallic" bonds with carbon.

Finally, all elements interact with carbon through physical forces, i.e., there is always a contribution from dispersion interactions. The bond energy produced by these forces is low, fractions or units of a kcal/mole. That is why the role of these forces is only appreciable in those systems where the level of the carbon-metal chemical interaction is low enough. The metals of the secondary B-subgroups of the periodic system of the fourth, fifth and sixth periods:

I gr.	II gr.	III gr.	IV gr.	V gr.	VI gr.
Cu	Zn	Ga	Ge	As	Se
Ag	Cd	In	Sn	Sb	Te
Au	Hg	Tl	Pb	Bi	Po

fall into this class.

For a high degree of the solid body wettability by liquid metals, intensive interfacial interaction is required. Such interaction favors the formation of bonds of metallic character. There-

fore formation at the interface of a new phase with metallic properties is preferable.

Thus the highest degree of graphite and diamond wetting by metals is to be expected for transition metals with d -electron band vacancies.

The intensity of the phase interaction (or the chemical reaction intensity) at high temperatures depends more on the nature of reacting atoms and of bonding forces between them than on the structure they form. Bonding forces between carbon atoms in the layers of the graphite lattice are weaker than in the diamond lattice. This is indicated by the low transition heat (diamond to graphite) of about 0.5 kcal/mole; however, the sublimation heat is about 17 kcal/mole.

The two forms of carbon differ little from one another energetically. This means that the energetic effect of chemical transformation in which graphite takes place should be close to that for those involving diamond. Thus heats of carbon combustion (reaction of carbon with oxygen) for diamond and graphite are close to one another (94.05 kcal/mole for graphite and 94.50 kcal/mole for diamond).

The reaction intensities of diamond and graphite with liquid metals are also close, i.e., we should expect similar metal wettability for both forms. This statement is confirmed experimentally [10] and permits the substitution of inexpensive graphite for diamond in trial studies.

Experimental data and characteristics concerning diamond and graphite wettability by metals are presented below.

While analyzing experimental data the metals being studied are divided into several subgroups in accordance with the types of bonds and the intensity and character of their interaction with carbon.

Metals of Secondary B-sub-groups of the Periodic System IV and VI-th Periods

These elements are practically inert to carbon. They do not form stable carbides [119,144]. In the liquid state up to the boiling point, they usually dissolve only small quantities of carbon (10^{-3} – 10^{-1} At.%) [125,135,138,155] and do not corrode graphite materials on long-term contact [136,137].

The wettability of graphite and diamond by copper, silver, gold, gallium, germanium, tin, antimony, and bismuth has been studied in this group [27,118,119,126,132]. These metals do not wet diamond and graphite. The bond energy (the work of adhesion between the liquid metal and the carbon surface) is low: 70–300 erg/cm^2 (0.5–1.9 kcal/mole; Table 8, Fig. 17). The work of ad-

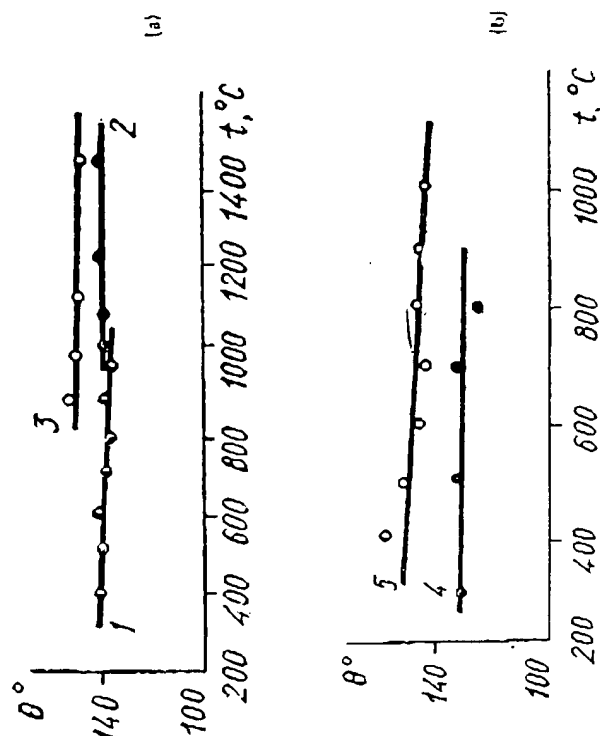


Fig. 16. a, b, Temperature dependences of wetting angles in the systems: 1-indium-diamond; 2-copper-graphite; 3-tin-graphite; 4-tin-diamond; 5-gallium-graphite.

TABLE 8. Wetting angles θ and the work of adhesion W_a of metals inert to carbon at the surface of diamond and graphite [27]

Liquid metal	t, °C	θ	W_a , erg/cm^2
Copper	1100	145	235
	1150	146	235
Silver	1000	120	450
Gold	1100	151	120
	1150	150	120
Indium	400	156	45
	500	152	60
Germanium	1000	142	100
	1000	136	115
Tin	1100	131	145
	1200	113	390
Lead	900	125	195
	1000	125	190
Antimony	1100	125	150
	1150	124	185
Bismuth	1000	110	265
	900	120	180
Graphite			
Copper	1100	140	315
Silver	1500	142	20
	980	136	255
Indium	800	141	105
Gallium	100	139	180
	1000	137	170
Germanium	1000	139	100
Tin	1000	149	65
Lead	1100	150	70
	800	138	75
Antimony	900	140	85
Bismuth	800	136	95

hesion is independent of temperature for the systems gallium-graphite, indium-diamond and tin-diamond but shows a slight decrease with increasing temperature for the system copper-graphite (Fig. 17).

If it is assumed that this interaction is of a chemical nature then, due to obvious endothermicity of the process, one should expect the increased interaction (an increased work of adhesion) intensity with temperature, which is not the case. This fact can be explained if one assumes that physical interactions are decisive

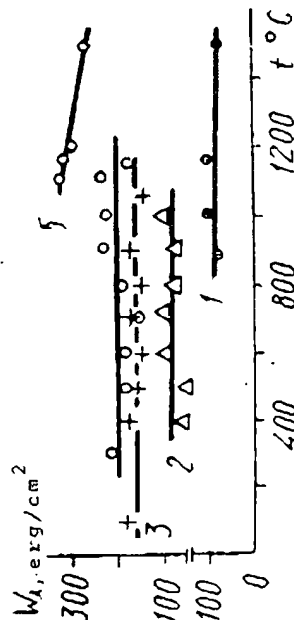


Fig. 17. Temperature dependences of adhesion work in the systems: 1-tin-diamond; 2-indium-diamond; 3-gallium-graphite; 4-tin-graphite; 5-copper-graphite.

for such systems (graphite, diamond, metals of the secondary B-sub-groups).

For the weakly interacting systems being considered here, a thermodynamic equilibrium contact of practically pure components (metal and carbon) exists and is characteristic in the temperature range under study. This means that the value of W_a (non-equil) in expression (4) is small.

With the help of the expression for the dispersion force potential, it is possible to quantitatively estimate the work of adhesion. The value of R in expression (II) is assumed approximately equal to $R_{Me} + R_C$ where R_{Me} and R_C are half the minimum interatomic distances in the metal and graphite respectively. Polarizability was approximately determined by the relation

$$\alpha \approx \frac{e^2 h^2}{4\pi^2 m I^2}$$

where h is the Planck constant, m is the electron mass and I is the first ionization potential.

The energy of interaction $W_a(\text{equil})$ per 1 sq.cm of the interface can be expressed in the following way.

$$W_a(\text{equil}) \approx nE$$

(n is a number of bonds metal-carbon per 1 sq.cm).

Since 1 sq.cm contains $0.345 \cdot 10^{16}$ carbon atoms in the diamond structure and $0.260 \cdot 10^{16}$ in the graphite structure and since for the metals studied this value fluctuates within the range $0.030 - 0.170 \cdot 10^{16}$ At/cm² then to a first approximation the number of bonds established at the liquid metal-carbon surface contact will be determined by the number of metal atoms. For this reason the value of n was calculated for each metal respectively.

As can be seen from the data of Table 9, a certain correspondence is observed between the calculated solid-liquid interfacial energies of interaction solid-liquid and the work of adhesion, W_a . At any rate dispersion interactions appears to be sufficient to explain the adhesion energy experimentally observed.

Transition Metals

The elements being studied (Ti, Ta, Cr, V, Mn, Nb, W, Mo, Fe, Co, Ni, Pd, Pt [27, 105, 126-134, 159], Zr [119], U [156], Ce [116], Zr, Ti, Nb, Mo [120-123], Ti, Zr [175, 176, 179, 184, 248], La, Ce, Pr, Nd [157], La [158], either in a pure form or in the form of additives to inert elements, show considerable adhesion activity on contact with graphite and diamond (Figs. 18-20, Table 10).

The work of adhesion of such metals and alloys at the graphite or diamond surface is large and reaches 2000-3000 erg/cm² or 20-25 kcal/mole when expressed on a unit volume basis.

Increasing temperature enhances the degree of diamond and graphite wettability by such metals (Fig. 21).

Wetting in such systems is determined by chemical interaction, carbide formation or dissolution of the solid in the liquid at the interface. Dispersion forces (units of kcal/mole) while clearly present in these systems, contribute insignificantly to the bond energy being observed (about 5-10%).

The results of the calculations of the work of adhesion and wettability in metal-graphite systems carried out by the formulae

TABLE 9. A comparison of calculated and experimental values of dispersion bond energies for the metal-carbon surface

Metal	$R_{me} \cdot 10^8$ cm	I , eV	$\alpha \cdot 10^{24}$ cm ³	E , erg/cm ²	W_a at 1000°C	
					erg/cm ²	erg/cm ²
					on diamond	on graphite
Cu	1.26	7.7	1.81	2.73	480	230
Ge	1.39	6.5	2.54	2.14	320	390
Ga	1.39	6.0	2.98	2.80	420	-
Ag	1.44	7.6	1.86	1.65	230	450
In	1.57	5.8	3.19	1.79	210	100
Al	1.44	9.2	1.27	1.33	185	120
Sn	1.58	7.3	2.02	1.21	140	190
Sb	1.61	8.5	1.49	0.95	105	180
Pb	1.75	7.4	1.96	0.81	75	263
Bi	1.82	7.2	2.07	0.72	65	-

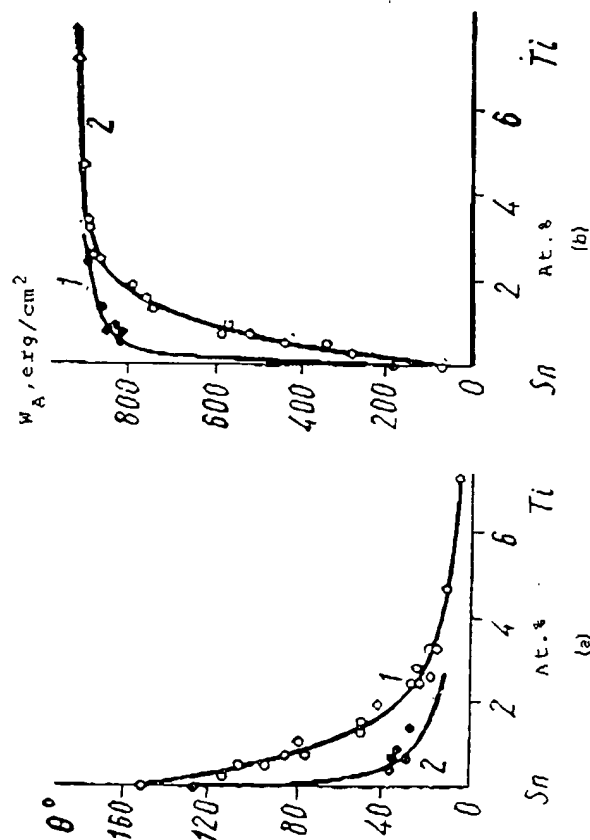


Fig. 18. a, b Concentration dependences of the wetting angle (a) and adhesion work (b) of tin-titanium alloys on graphite (1) and diamond (2) (1150°C).

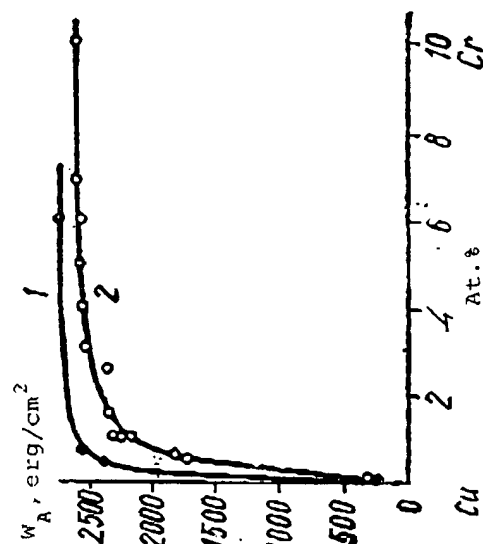


Fig. 19. Concentration dependences of adhesion work of copper-chromium alloys to diamond at (1) 1150°C and graphite (2) at 1250°C.

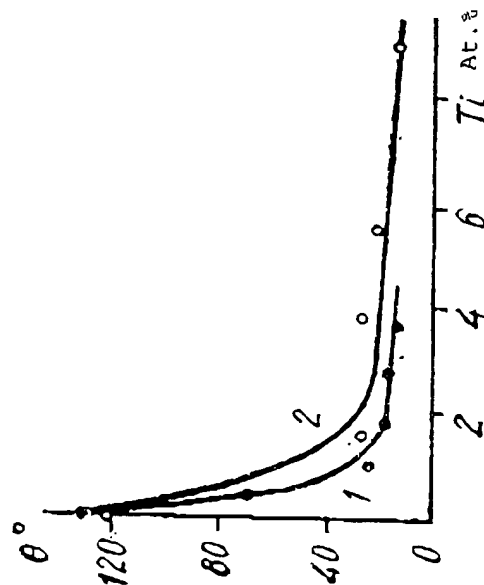


Fig. 20. Angle of contact of wetting diamond (1) and graphite (2) by eutectic alloy 40At.% Cu-60At.% Ag with titanium addition.

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Table 10 (continued)

Diamond and graphite wettability by aluminium, silicon and boron

Liquid metal, At%	t°C	θ	W_a erg/cm ²	Reference
Solid surface-diamond				
Cu+12.8 Ti	1150	0	2660	[10]
Sn+0.5 Ti	1150	38	855	"
Sn+2.5 Ti	1150	22	865	"
Ag+0.1 Ti	1000	45	1555	"
Ag+0.45 Ti	1000	5	1815	"
Cu+0.37 Cr	1150	37	2390	"
Cu+6 Cr	1150	0	2660	"
Au+5 Ta	1150	30	2200	[126]
Solid surface-graphite				
Cu+6.3 Ti	1150	30	2450	[10]
Cu+10 Ti	1150	0	2660	"
Sn+0.9 Ti	1150	76	560	"
Sn+7 Ti	1150	5	900	"
Ag+0.1 Ti	1000	85	990	"
Ag+1.0 Ti	1000	7	1810	"
Cu+0.6 Cr	1150	84	1380	"
Cu+6 Cr	1150	40	2330	"
Cu+10.2 Cr	1250	0	2620	"
Cu+24 Mn	1200	70	1780	"
Cu+5 Co	1200	138	335	"
Cu+10 Ni	1500	139	310	"
Cu+20 Mo	1500	134	375	[10]
Cu+6.2 V	1200	60	660	"
(Cu+9.3Ni)+6.2V	1200	50	2490	"
(Cu+9.3Ni)+7Nb	1200	40	2390	"
(79Cu+21Ni)+Mo*	1400	100	950	"
(51Cu+39Ni+105Si)+W*	1470	61	1800	"
La	900	45	1220	[157]
Ce	1090	13	1530	"
Pr	920	20	1310	"
Nd	1000	10	1185	"
Ti	1800	0	2920	[122]
Fe	1550	37	3340	[10]
Co	1500	48	3200	"
Ni	1500	45	2985	"
Pd	1560	44	2500	"
Pt	1800	87	1830	"
Fe+15.7 C	1550	107		[10]
Co+15.5 C	1550	120		"
Ni+13 C	1550	115		"
Pd+C**	1560	116		"
Fe+32 V	1550	35		[254]
Fe+53 V	1550	0		[254]

*The concentration of tungsten and molybdenum in the melt is unknown.

TABLE 10. Diamond and graphite wetting by alloys containing transition elements and with pure transition metals

Liquid metal, At%	t°C	θ	W_a erg/cm ²	Reference
Solid surface-diamond				
Cu+12.8 Ti	1150	0	2660	[10]
Sn+0.5 Ti	1150	38	855	"
Sn+2.5 Ti	1150	22	865	"
Ag+0.1 Ti	1000	45	1555	"
Ag+0.45 Ti	1000	5	1815	"
Cu+0.37 Cr	1150	37	2390	"
Cu+6 Cr	1150	0	2660	"
Au+5 Ta	1150	30	2200	[126]
Solid surface-graphite				
Cu+6.3 Ti	1150	30	2450	[10]
Cu+10 Ti	1150	0	2660	"
Sn+0.9 Ti	1150	76	560	"
Sn+7 Ti	1150	5	900	"
Ag+0.1 Ti	1000	85	990	"
Ag+1.0 Ti	1000	7	1810	"
Cu+0.6 Cr	1150	84	1380	"
Cu+6 Cr	1150	40	2330	"
Cu+10.2 Cr	1250	0	2620	"
Cu+24 Mn	1200	70	1780	"
Cu+5 Co	1200	138	335	"
Cu+10 Ni	1500	139	310	"
Cu+20 Mo	1500	134	375	[10]
Cu+6.2 V	1200	60	660	"
(Cu+9.3Ni)+6.2V	1200	50	2490	"
(Cu+9.3Ni)+7Nb	1200	40	2390	"
(79Cu+21Ni)+Mo*	1400	100	950	"
(51Cu+39Ni+105Si)+W*	1470	61	1800	"
La	900	45	1220	[157]
Ce	1090	13	1530	"
Pr	920	20	1310	"
Nd	1000	10	1185	"
Ti	1800	0	2920	[122]
Fe	1550	37	3340	[10]
Co	1500	48	3200	"
Ni	1500	45	2985	"
Pd	1560	44	2500	"
Pt	1800	87	1830	"
Fe+15.7 C	1550	107		[10]
Co+15.5 C	1550	120		"
Ni+13 C	1550	115		"
Pd+C**	1560	116		"
Fe+32 V	1550	35		[254]
Fe+53 V	1550	0		[254]

*The concentration of tungsten and molybdenum in the melt is unknown.

cited in Chapter 1 are presented in Table 11. Within an order of magnitude, there is a good correspondence between calculated and experimental values of the work of adhesion.

The adhesion activity of transition metals varies considerably. It can be related with the extent to which the metallic d-band is empty. In alloys formed with copper and gallium [101,105], the wetting activity of alloys with the IVth period elements (titanium, vanadium, chromium, manganese, cobalt and nickel) has been studied.

The adhesion activity as a whole decreases from titanium to nickel (Figs. 22,23) and corresponds to an increase in the filling of the elemental d-band. The work of adhesion of nickel, cobalt and iron in the pure form decreases from iron to nickel: 3340, 3200 and 2985 erg/cm², respectively.

For the Vth period the elements studied can be arranged in the order: Zr, Nb, Mo, Rb, Pd, with their decreasing adhesion activity coinciding with the filling of the d-band [10].

On comparing the wetting activity of elements, as with any additive to any solvent, the thermodynamic activity of the element in an alloy is to be taken into account. This is considered in reference [252] where the sharply differing wetting activity of manganese dissolved in various solvents is observed. In copper,

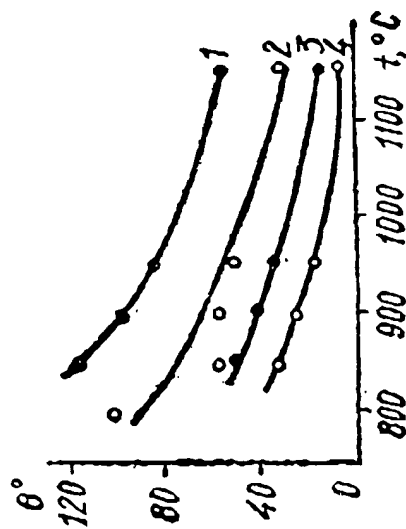


Fig. 21. Temperature dependences of the angle of contact of wetting graphite by tin-titanium alloys. 1-1.3; 2-2.46; 3-4.6; 4-7At.% Ti.

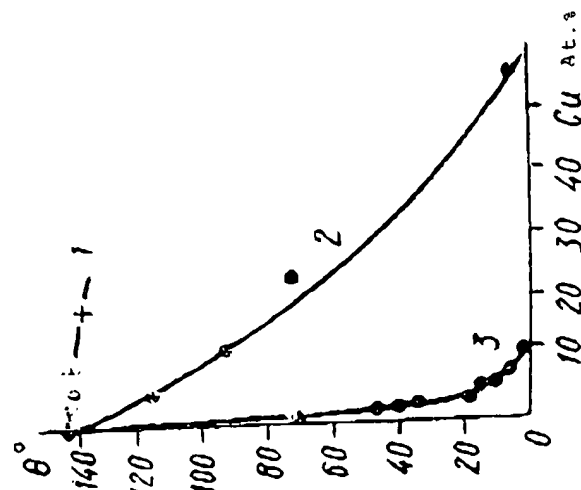


Fig. 22. Wettability of graphite by alloys of copper with nickel and cobalt at 1300-1500°C (1) with manganese at 1200°C (2) and chromium at 1250°C (3).

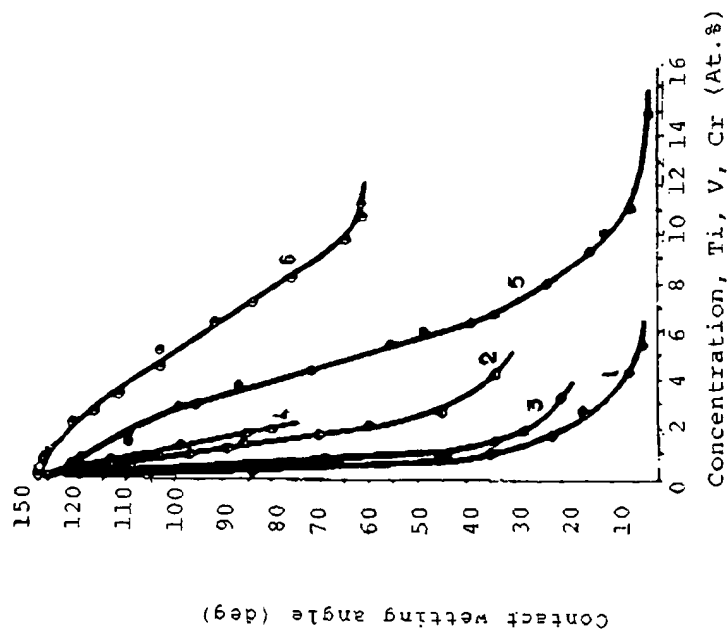


Fig. 23. Wettability of graphite by gallium-titanium (1,2), gallium-vanadium (3,4) and gallium-chromium (5-6) melts at 1050°C (1,3,5) and 900°C (2,4,6).

silver and tin where the thermodynamic activity of manganese is close to its concentration, the addition of manganese decreases the wetting angle. However, on adding different quantities of manganese to gold and germanium the alloys have very low graphite wettability and this does not improve until concentrations of up to 40-50 at.% of manganese are added (Fig. 24).

For rare-earth elements, considerable adhesion affinity for diamond and graphite surfaces is observed. In the pure form La, Ce, Pr, Nd [157], Y, La [158] form small wetting angles at graphite surface (Table 10).

The role of solid-liquid phase interactions in wettability phenomena is well illustrated by the systems graphite-metal of the VIIIth group of the periodical system.

In non-equilibrium systems when graphite is in contact with a pure metal (iron, nickel, cobalt, palladium, platinum) and carbon dissolution is taking place at the interface, the wetting angle is small (20-30°) and the work of adhesion is large (~3000 erg/cm²). For the same metals saturated under conditions close to those at equilibrium, the wetting angle increases (120°) and the work of adhesion decreases by a factor of three (to 1000 erg/cm²). Under such conditions (those of equilibrium) the contribution to the adhesion work W_a chem.non-equil disappears.

Metals Forming Covalent Bonds with Carbon.

In this group silicon, germanium, aluminum and boron [116, 118, 119, 27] have been studied. In the pure form these metals wet graphite (diamond) and the work of adhesion reaches approximately 1000-1200 erg/cm² (about 10 kcal/mole). These values, however, are still less than the maximum values of the various bond energies with graphite or diamond (about 2000-1000 erg/cm²). This means a lower heat of reaction for carbide formation for the given metals compared to those obtained with the transition metals (for example, 12.4 kcal/mole for SiC and 45.5 kcal/mole for TiC). In copper al-

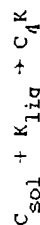
loys the adhesive activity of boron [27] and silicon [253] on graphite has been studied. Wettability occurs (θ ~ 40°) at a concentration of 5 at.% for boron and 40 at.% for Si.

Metals Forming Ionic Bonds with Carbon

Quantitative data on graphite wettability by alkali and alkaline-earth metals are available for lithium [115] (at 300°C, θ = 80°). It is also known that at temperatures higher than 450°C sodium forms a wetting angle of less than 90° [136] on graphite. Alkali metals corrode graphite surfaces on prolonged contact [113, 136, 137].

On contact of graphite with alkali metals the formation of metal polycarbides of MeC₈, MeC₁₆ type takes place with negative heats of reaction (though with low absolute values).

For instance, for reaction of graphite with liquid potassium



ΔH = -1500 kcal/g - atom of carbon [114].

Taking into account the low values of alkali metal surface tensions (100-400 dyne/cm) and negative values of the reaction heat it may be assumed that in these systems wettability should be generally observed (wetting angle not less than 90°). This is found to be true for lithium and sodium.

There is no data available in the literature about the wetting properties of alkaline-earth metals on graphite and diamond. High negative values of the heats of formation of carbides with the appropriate metals (-28.7 kcal/mole for BeC₂; -7 kcal/mole for CaC₂; -6 kcal/mole for BaC₂) should result in small wetting angles for these systems. The relationship between the adhesion of a solidified liquid metal melt to a solid phase and the mechanical strength of the contact between the solidified metal and the solid body surface is of practical importance and has been studied for metal-diamond systems in a number of works [10, 248].

2. The wettability of covalent high-melting carbides, borides and nitrides by liquid metals (SiC , B_4C , BN , Si_3N_4).

The analysis of wettability in the systems formed by metal and binary compounds can be, to a first approximation, carried out by considering the interactions between the liquid metal and each kind of components atoms of the solid phase (in cases considered here, with silicon and carbon for SiC , with carbon and boron for B_4C , and with nitrogen and silicon for Si_3N_4 , all as if each substance was in a pure state). The actual intensity of the interaction of the metal and the compound will, of course, be weakened by the bonding between the components in the compound lattice [10].

Systems: inactive metal - SiC . From the metals of secondary subgroups of the elements of the periodic table (periods IV-VI) the following elements have been studied in contact with silicon carbide: Cu, Au, Ag, In, Ge, Ga, Sn. These metals are inert to carbon. In this subclass of elements only copper, arsenic and selenium form chemical compounds with silicon which are stable [125,181]. The rest of the metals form either simple eutectic systems with silicon in the absence of solubility in the solid state or form immiscible systems. Germanium and silicon form a system with unlimited mutual near-ideal solubility [181] (Table 15). In such systems positive or close to zero heat of alloy formation is observed, i.e. definitely less than the heat of SiC formation (equal to 15.2 kcal/mole according to the data of [195] and to 12.4 kcal/mole according to [18]).

Thus the level of chemical interaction of such metals as Au, Ag, In, Sn, Ga, Ge with SiC is insignificant. This results in a low adhesion energy, high wetting angles and a virtual independence of these values on temperature. All of this is confirmed by experimental data [10,57,190,191] (Fig. 23, Table 12).

There are data cited in [57] for the wettability of silicon carbide and silicon nitride by liquid alloys; at 1100°C wetting angles are 165 and 164°, respectively. Obtuse wetting angles on

TABLE 12. The wetting angles and work of adhesion in the systems metal - silicon carbide

Metal	t, °C	θ°	W_a , erg/cm ²	Reference
<i>Elements non-interacting with carbon and weakly interacting with silicon</i>				
Ag	1100	128	350	[190]
Au	1150	138	260	"
Ga	800	118	350	"
In	800	130	175	"
Ge	1050	113	365	"
Sn	1050	135	145	"
Sn	1100	165	80	[57]
<i>Elements forming carbides and silicides</i>				
Cu	1100-1250	Interaction at the interface, [10] Formation of intermediate phases [191]; wetting		
Al	1100	34	1450	[190]
Ni	1460, 1 sec.	65	2500	[190]
Si	1480	36	1320	[190]

aluminum nitride and silicon nitride form with metals of the iron group: copper, aluminum, tin and silver. Silicon nitride is wetted ($0 < 90^\circ$) by silicon and calcium [185,186,188].

Systems: inactive metal-boron carbide. Most of the metals of the secondary group of the IV-VIth periods show low reactivity relative to boron (Table 15). A certain amount of boron dissolves in copper [40,192]. It is known [40,192] that germanium forms an unstable compound GeB_4 . Such elements as Cu, Ag, Ge, Sn studied in contact with boron carbide have rather low chemical affinity for boron. This affinity is much lower than that of boron and carbon in the solid phase substance, B_4C : 12.2 kcal/mole.

As has been already mentioned carbon does not contribute significantly to the chemical portion of the adhesion energy with metals from the subclass listed here. This allows us to understand the low values of the work of adhesion observed during investigations (150-380 erg/cm²) and the high wetting angles [10] (Table 13, Fig. 25).

TABLE 13. Wettability of boron carbide B_4C by liquid metals

Metal	$t, ^\circ C$	$\theta, ^\circ$	$W_a, \text{erg/cm}^2$	Reference
<i>Elements inactive to carbon and weakly interacting with boron</i>				
Cu	1100	136	380	[10]
Ag	1300	137	240	"
Ge	1100	130	255	"
Sn	1100	135	140	"
<i>Elements forming carbides and borides</i>				
Al	1150 (5 min.)	33	1500	[10]
Si	1430	0	1600	"
Ni	1500	87	1845	"
Co	1500	46	3150	"
Fe	1500	36	3310	"
Cu+5% Cr	1150	30	-	"
Sn+5% Ti	1000	0	-	"
Cr	1900	0	-	[177]

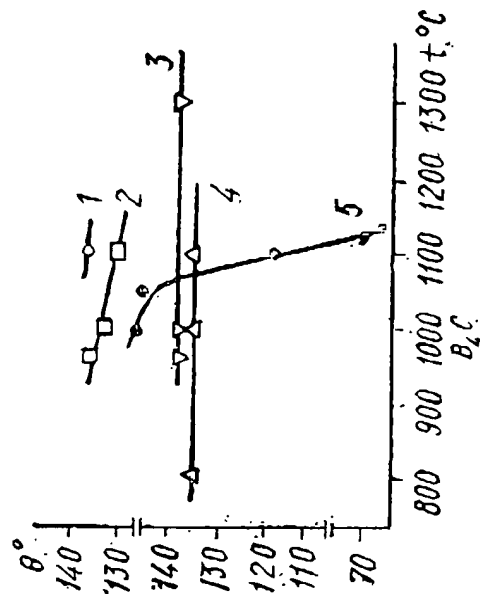


Fig. 25. Wettability of boron carbide by liquid metals 1-Cu; 2-Ge; 3-Ag; 4-Sn; 5-Al.

Systems: inactive metal-boron nitride. Compounds with nitrogen and such metals as copper, silver, gold, indium and tin are unstable (their heat of formation has either a small positive or small negative value) they decompose or even explode with gentle heating. Stable nitrides are formed by either silicon or gallium. However their heat of formation (45 and 25 kcal/mole respectively) is much less than that of boron nitride (60 kcal/mole). Only aluminum forms a compound which has a greater heat of formation than boron nitride (see Table 15).

Such elements as silver, gold, gallium, indium and tin essentially do not fuse with boron. For this reason it may be assumed that at the interface between copper (silver, gold, germanium, gallium, indium and tin) and boron nitride there is little chemical activity. Because of this, high values of wetting angles and low adhesion of these metals to boron nitride [10,196,197] can be observed (Fig. 26, Table 14). The systems lead-aluminum nitride (wetting angle is 143° at $540^\circ C$) and silver-aluminum nitride (wetting angle is 133° at $1000^\circ C$ [250,251]) belong to such systems.

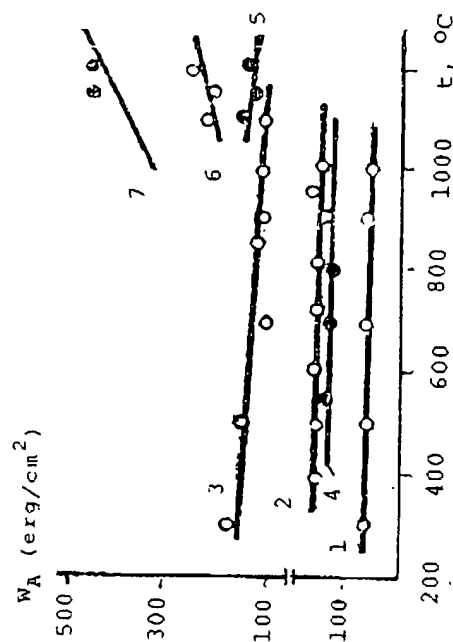


Fig. 26. Adhesion of hexagonal (1-Sn, 6-Cu) and cubic boron nitride (2-In, 3-Sn, 4-Ga, 5-Ge, 7-Cu) to liquid metals.

TABLE 14. The wetting angles and work of adhesion of liquid metals on the surface of cubic and hexagonal boron nitride [10]

Liquid metal	Cubic boron nitride		Hexagonal boron nitride	
	t, °C	θ°	t, °C	θ°
Elements weakly interacting with boron and nitrogen				
Copper	1100	137	360	1100 146
Silver	1000	146	160	1000 140
Gold	1100	145	175	-
Boron	-	-	-	2200 133
Gallium	1100	130	225	-
Indium	1000	110	300	1000 136
Germanium	1100	138	175	1100 139
Tin	1100	137	115	1000 150
Elements actively interacting with boron and nitrogen				
Silicon	1500	95	855	1500 110
Aluminum	1100	60	1220	1100 <90
Cobalt	-	-	-	1500 35
Nickel	-	-	-	1500 75

From the systems studied one can single out those in which the liquid metal has a low chemical affinity for the component atoms of the solid phase (to be more exact those having a lower affinity than the mutual affinity of the components and interacting rather weakly with the crystal surfaces of such compounds).

Small values of the work of adhesion are observed (50-400 erg/cm² or 0.1-1.5 kcal/mole) and are almost unaffected by either temperature or time of contact and evidently have "non-chemical" origin.

Physical, van der Waals, forces (dispersion interactions) can be responsible since this interaction is small and of the correct magnitude (fractions or units of kcal/mole). Such forces become apparent despite their universality, only for non-reacting systems.

It is rather difficult to obtain an exact value of the bond energy as has been done previously for the metal-graphite system, since effective ionization potentials and the atomic (ionic) size of the atoms/ions size in crystals of carbides and nitrides are

TABLE 15. The Character of Metal Interaction with Boron, Nitrogen, Carbon, and Silicon

Metal	Boron [192]	Nitrogen	Silicon [181]	Carbon
Cu	Liquid copper dissolves 10 wt. % at 1100°C	Compound Cu ₃ N (ΔH ₂₉₈ = -17.8 kcal/mole) decomposes at heating with explosion [125, 78].	Formation of silicides CuSi and Cu ₂ Si, which decompose at heating with explosion. In-eutectic diagram without solubility in the solid state. Eutectic point at 1050°C, there is strongly shifted to Ga.	Complete mutual solubility in the solid and the liquid state. Eutectics without solubility in the solid state. Eutectic point is strongly shifted towards ctn.
Ag	No alloys are formed	Compound Ag ₃ N (ΔH ₂₉₈ = -79 kcal/mole) decomposes at heating with explosion [125, 78].	The same	Complete mutual solubility in the solid and the liquid state. Eutectics without solubility in the solid state. Eutectic point is strongly shifted towards ctn.
Sn	No alloys are formed	Compound Sn ₃ N (ΔH ₂₉₈ = -4.6 kcal/mole) is formed only at reaction with ammonia [195, 78].	Compound GaN (ΔH ₂₉₈ = -25 kcal/mole) is formed only at reaction with ammonia [195, 78].	Complete mutual solubility in the solid and the liquid state. Eutectics without solubility in the solid state. Eutectic point is strongly shifted towards ctn.
Ga	Compound is formed	Compound Ge ₃ N (ΔH ₂₉₈ = -39 kcal/mole) [189, 194].	Compound GaN (ΔH ₂₉₈ = -25 kcal/mole) is formed only at reaction with ammonia [195, 78].	Complete mutual solubility in the solid and the liquid state. Eutectics without solubility in the solid state. Eutectic point is strongly shifted towards ctn.
Al	Liquid aluminum is a compound SiB ₂ at 1500°C. There are compounds AlB ₂ and AlB ₁₂ .	Compound AlN (ΔH ₂₉₈ = -76.5 kcal/mole) dissolves 8 wt. % at 1500°C. There are compounds AlB ₂ and AlB ₁₂ .	Compound AlN (ΔH ₂₉₈ = -76.5 kcal/mole) dissolves 8 wt. % at 1500°C. There are compounds AlB ₂ and AlB ₁₂ .	Complete mutual solubility in the solid and the liquid state. Eutectics without solubility in the solid state. Eutectic point is strongly shifted towards ctn.

not known. These dimensions however can be given an approximate value (as close as possible to the true value) such that the character and direction of bond energy changes from one metal to another for the same type of solid phase.

For such calculations the following expression has been used:

$$E = N_{Me} \cdot \frac{3}{2} \frac{\alpha_1 \alpha_2 \cdot I_1 \cdot I_2}{R(I_1 + I_2)},$$

where N_{Me} is the number of metal atoms per unit surface area. It was assumed that $R = R_{Me} + K_1$, where R_{Me} is the metallic atomic radius equal to one half of the least interatomic distance in the structure of metal. K_1 is a constant characterizing the distance from the atom to the high-melting phase surface

$$N_{Me} \sim \frac{1}{R_{Me}^2}; \quad \alpha = \frac{e^2 R^2}{4\pi m I^2}; \quad d \sim \frac{1}{I^2}$$

(e and m are the electron charge and mass, h is Plank constant).

Then

$$E = A \frac{1}{I_{Me}(I_{Me} + K_2)(R_{Me} + K_1)^6 R_{Me}^2} = A\phi \quad (23)$$

An analysis of this dependence allows us to arrange the metals in the order of their changing potentials due to dispersive interaction with the solid surface. In particular, within a group of the periodic table, for metals of the secondary group of the IV-VI periods, the following sequence of decreasing dispersion bond energies can be listed: $Cu > Ag > Au, Ga > In > Tl, Ge > Sn > Pb$. The values of ϕ are proportional to the dispersion potential of the metallic element with respect to the same solid substance (SiC) are given in Table 16. Calculations have been carried out using $K_1 = 1.34 \cdot 10^8$ cm and $K_2 = 8.1$ eV (for the radius and the ionization potential of the silicon atom).

Thus, it should be expected that the degree of wettability (or

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TABLE 16. Values of interaction dispersion potentials between the metal and the solid surface (exact except for the constant)

I group		III group		IV group	
Element	$\phi \cdot 10^{-57}$ eV $\cdot 2 \cdot \text{cm}^{-64}$	Element	$\phi \cdot 10^{-57}$ eV $\cdot 2 \cdot \text{cm}^{-64}$	Element	$\phi \cdot 10^{-57}$ eV $\cdot 2 \cdot \text{cm}^{-64}$
Cu	15.3	Ga	14.6	Ge	9.4
Ag	8.8	In	8.4	Sn	5.7
Au	6.6	Tl	5.0	Pb	3.3

the work of adhesion would decrease as we proceed within a group from the top to the bottom of the periodic table. A similar dependence can be observed for both diamond and graphite and in general for nonmetallic crystals such as oxides and sulphides.

The adhesion energies of liquid metals to the surface of boron carbide, silicon carbide, boron nitride (hexagonal and cubic) as well as to that of diamond and graphite are compared in Fig. 27 and indicate a dependence on the site of the element in a given group in the periodic table. As is seen from the figure, there is decrease in the work of adhesion of the metals of groups I, III and IV as we proceed from the top to the bottom of the table. The opposite direction of change of W_a is observed only in three pairs of fourteen sequences (fifty pairs in all): Sn-Pb for graphite, Cu-Ag for diamond and Ag-Au for boron nitride (dashed line in Fig. 27). Evidently this should be attributed to experimental error. The latter may be large for such nonreactive systems and small values of adhesion energies are subject to the influence of trace amounts of additives and impurities both in the metal and solid phases and at the contact surface.

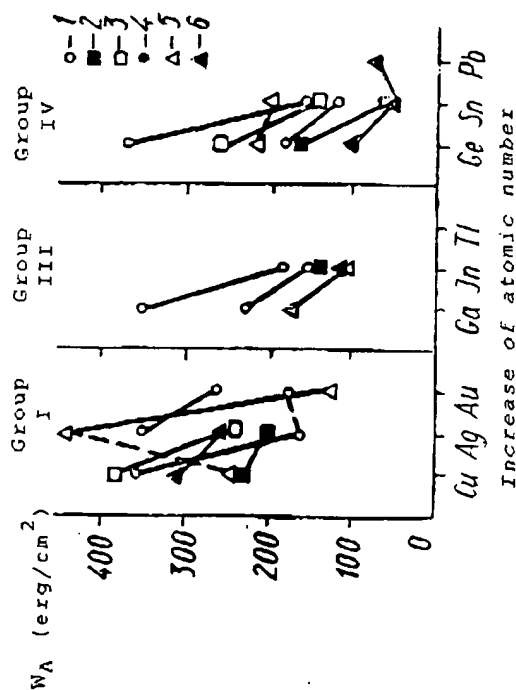


Fig. 27. Adhesion in the system covalent crystal-metal of side B-subgroups of the periodic system depending on the metal cation in the group ($T=1000-1100^{\circ}\text{C}$): 1-BN(cubic), 2-BN(hexag.), 3-B₄C, 4-SiC, 5-diamond, 6-graphite.

Systems with Chemically Active Metals

From Tables 12, 15 and 15 it follows that metals with substantial chemical affinity to the elements constituting the solid phase (boron, nitrogen, carbon, silicon) will readily wet the solid compounds under study. Such elements are aluminium and silicon, metals of the iron group, chromium and titanium.

With the formation of a reaction zone, metals of the iron group in the solid and liquid state exhibit moderate interaction with silicon carbide surface. Wetting angles of these metals range from $45-90^{\circ}$ on silicon carbide surfaces at $1500-1600^{\circ}\text{C}$; that for melted chromium is 5° [189]. Nickel, cobalt and iron at 1600°C interact vigorously with B₄C [10], liquid chromium spreads completely over the carbide B₄C surface [177].

The degree of wettability of solid carbides, borides or ni-

trides depends on the relative values of the heats (or better free energies) of formation of metal-solid compounds and of the solid compound itself. Thus the contact angles of boron nitride wetted by aluminium and silicon are 60 and 90° , respectively according to reference [196] (Figs. 28, 29), i.e. aluminium wets boron nitride better, in accordance with the higher heat of formation of aluminium nitride AlN (-76.5 kcal/g-atom of nitrogen) [78]. At the same time the wettability of silicon carbide by aluminium and silicon differ very little ($\theta_{\text{Al-SiC}} = 34^{\circ}$, $\theta_{\text{Si-SiC}} = 36^{\circ}$). This would be expected from the approximately same heat of formation of silicon carbide and aluminium carbide (-12 and -12.4 kcal/g-atom of carbon, respectively). Contact angles on wetting boron with silicon and aluminium are also close. At its melting point silicon spreads over B₄C with a wetting angle close to zero. Aluminium at 1150° and a 5 minute exposure exhibits an angle of 33° and a tendency to spread further [10]. In line with the above reasoning, it is assumed that the interaction of silicon and aluminium with nitrogen and carbon is determining as compared to these elements interactions with boron and silicon. Really, aluminium and silicon nitrides and carbides are more stable than the corresponding borides. This is even more true when they are compared to the silicides. By forming reasonably stable silicides, copper interacts with silicon carbide and wets it after a long-term

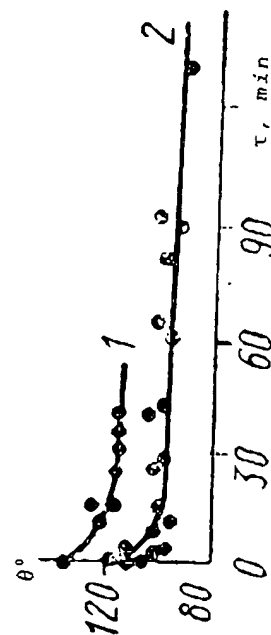


Fig. 28. Wetting angle of silicon at the surface of hexagonal (1) and cubic (2) boron nitride depending on time.

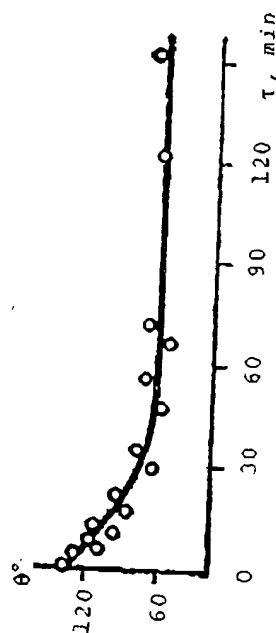


Fig. 29. Aluminum spreading over boron nitride.

contact (it is difficult to measure the wetting angle because of a two phase metal melt and the distorted form of the liquid surface). Liberation of free carbon, the product of the reaction of copper with silicon carbide [10,191], is observed at the surface of the liquid phase.

The system Si-SiC should be considered separately. Unlike the systems Ni-SiC and Cu-SiC, for instance, where interaction is rather intensive, the system Si-SiC is stable and in spite of high temperature (up to 1580°C) long-term exposure (up to one and a half hours) the wetting angle tends to increase with increasing temperature and exposure. Evidently this is brought about by the fact that at temperatures close to the silicon melting point the latter dissolves small amounts of carbon, i.e. practically pure silicon and silicon carbide form the equilibrium system.

Evidently the system B-BN where boron forms a large wetting angle (-134° at $T = 2200^\circ$) [10] (Table 14) is similar to the system Si-SiC. The phase diagram of this system has not yet been developed; one can only assume that liquid boron in contact with BN forms a near-equilibrium system.

While comparing wetting properties of such compounds as BN, B₄C and SiC one can notice the regular increase of wetting by metals of these compounds in the order given. This was observed for all of the metals under study. Table 17 shows a comparison of the metal wettability of these compounds. This order of wetting

TABLE 17. Contact angles of wetting of covalent carbide and boride surfaces by metals

Covalent crystal	ΔH_{2981} Kcal/mole	θ°					
SiC	-12.4	Wetting, corrosion of the surface	129	116	110	138	130
B ₄ C	-12.2	136	137	-	130	-	135
BN ^{cub}	-60.0	137	146	130	138	145	137
BN ^{hecsag.}	-60.4	146	140	-	139	-	150
						136	136
						75	110
						-	-
						60	33
						87	0
						65	36
						130	34
						51	Al
						Ni	
						In	
						Sn	
						Au	
						Ge	
						Ga	
						Ag	
						Cu	

Compound	Metal	t°C	Atmosphere	θ°	Reference
Cr ₃ C ₂	Ni	1500	Argon	0	[16]
	Ni	1500	Vacuum	0	[165]
Cr ₃ C ₃	Cu	1100	"	47	[165]
	Cu	1150	"	44	[10]
HfC	Cu	1100-1200	Vacuum	132-132	[16]
	Ni	1380	"	23	[165]
NbC 0.97	Ni	1380	"	18	[178]
	Cu	1100-1200	Vacuum	70-48	[165]
Mo ₂ C	Ni	1420	"	14	[178]
	Cu	1100-1200	Vacuum	18-0	[167]
Cr ₃ C ₂	Ni	1500	Argon	0	[16]
	Ni	1500	Vacuum	0	[165]
HfC	Ni	1380	"	23	[165]
	Argon	1450	Argon	37	[178]
NbC 0.97	Ni	1380	"	18	[178]
	Cu	1100-1200	Vacuum	70-48	[165]
Mo ₂ C	Ni	1420	"	14	[178]
	Cu	1100-1200	Vacuum	18-0	[167]
Cr ₃ C ₂	Ni	1500	Argon	0	[16]
	Ni	1500	Vacuum	0	[165]
HfC	Ni	1380	"	23	[165]
	Argon	1450	Argon	37	[178]
NbC 0.97	Ni	1380	"	18	[178]
	Cu	1100-1200	Vacuum	70-48	[165]
Mo ₂ C	Ni	1420	"	14	[178]
	Cu	1100-1200	Vacuum	18-0	[167]
Cr ₃ C ₂	Ni	1500	Argon	0	[16]
	Ni	1500	Vacuum	0	[165]
HfC	Ni	1380	"	23	[165]
	Argon	1450	Argon	37	[178]
NbC 0.97	Ni	1380	"	18	[178]
	Cu	1100-1200	Vacuum	70-48	[165]
Mo ₂ C	Ni	1420	"	14	[178]
	Cu	1100-1200	Vacuum	18-0	[167]
Cr ₃ C ₂	Ni	1500	Argon	0	[16]
	Ni	1500	Vacuum	0	[165]
HfC	Ni	1380	"	23	[165]
	Argon	1450	Argon	37	[178]
NbC 0.97	Ni	1380	"	18	[178]
	Cu	1100-1200	Vacuum	70-48	[165]
Mo ₂ C	Ni	1420	"	14	[178]
	Cu	1100-1200	Vacuum	18-0	[167]
Cr ₃ C ₂	Ni	1500	Argon	0	[16]
	Ni	1500	Vacuum	0	[165]
HfC	Ni	1380	"	23	[165]
	Argon	1450	Argon	37	[178]
NbC 0.97	Ni	1380	"	18	[178]
	Cu	1100-1200	Vacuum	70-48	[165]
Mo ₂ C	Ni	1420	"	14	[178]
	Cu	1100-1200	Vacuum	18-0	[167]
Cr ₃ C ₂	Ni	1500	Argon	0	[16]
	Ni	1500	Vacuum	0	[165]
HfC	Ni	1380	"	23	[165]
	Argon	1450	Argon	37	[178]
NbC 0.97	Ni	1380	"	18	[178]
	Cu	1100-1200	Vacuum	70-48	[165]
Mo ₂ C	Ni	1420	"	14	[178]
	Cu	1100-1200	Vacuum	18-0	[167]
Cr ₃ C ₂	Ni	1500	Argon	0	[16]
	Ni	1500	Vacuum	0	[165]
HfC	Ni	1380	"	23	[165]
	Argon	1450	Argon	37	[178]
NbC 0.97	Ni	1380	"	18	[178]
	Cu	1100-1200	Vacuum	70-48	[165]
Mo ₂ C	Ni	1420	"	14	[178]
	Cu	1100-1200	Vacuum	18-0	[167]
Cr ₃ C ₂	Ni	1500	Argon	0	[16]
	Ni	1500	Vacuum	0	[165]
HfC	Ni	1380	"	23	[165]
	Argon	1450	Argon	37	[178]
NbC 0.97	Ni	1380	"	18	[178]
	Cu	1100-1200	Vacuum	70-48	[165]
Mo ₂ C	Ni	1420	"	14	[178]
	Cu	1100-1200	Vacuum	18-0	[167]
Cr ₃ C ₂	Ni	1500	Argon	0	[16]
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	Ni	1500	Vacuum	0	[165]
HfC	Ni	1380	"	23	[165]
	Argon	1450	Argon	37	[178]
NbC 0.97	Ni	1380	"	18	[178]
	Cu	1100-			

Compound	Metal	t°C	Atmosphere	θ°	Reference
Zn-C	Bi	700-1100	"	140-52	[55]
	Ni	1380	Vacuum	0	[165]
	Co	1500	Hydrogen	0	[48]
	Co	1500	"	0	[161]
	Co	1420	Vacuum	0	[165]
	Co	1300	"	90	[178]
	Cu	1100	Vacuum	135	[55]
	Cu	1100-1500	Argon	140-118	[55]
	Cu	1100-1200	Vacuum	127-125	[165]
	Si	1500	"	22	[178]
	Ni	1380	"	24	[165]
	Ni	1450	"	32	[178]
TiB ₂	Ni	1480	Helium	38.5	[166]
	Ni	20 mln	Vacuum	0	[186]
	Ni	1500	Argon	150-114	[166]
	Cu	1100-1400	Argon	131-122	[166]
VB ₂	Cu	1100-1400	Argon	131-122	[166]
	Cu	1100-1400	Argon	131-122	[166]
	Cu	1100-1400	Argon	131-122	[166]
	Cu	1100-1400	Argon	131-122	[166]
	Cu	1100-1400	Argon	131-122	[166]
	Cu	1100-1400	Argon	131-122	[166]
	Cu	1100-1400	Argon	131-122	[166]
	Cu	1100-1400	Argon	131-122	[166]
	Cu	1100-1400	Argon	131-122	[166]
	Cu	1100-1400	Argon	131-122	[166]
	Cu	1100-1400	Argon	131-122	[166]
	Cu	1100-1400	Argon	131-122	[166]
VC 0.88	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
VC	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
Zn-C	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]
	Ni	1480	Helium	100	[166]

Table 18 (continued)

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can be attributed to a lower thermodynamic strength of SiC and B_4C compared to that of BN (lower formation heat).

C. The Wettability of High-Melting Metal-Like Compounds by Metals

Metals

The wettability of metallike carbide, boride and nitride phases by metals has been studied in a number of works [10,16,55,160-174, 178,180,249-251]. The data are summarized in Table 18. In general metallike compounds are wetted better than covalent ones. Thus the wetting angles of nickel at the surface of SiC , B_4C and BN are approximately 65, 37, and 75° while at the surface of metallike phases they range from 0 to 30°. This indicates the extent of the metallic character of the solid phase and a rather high value of W_a (equil). Nontransition metals wet metallike compounds much worse than transition metals. Nevertheless in some systems these metals form quite small wetting angles (less than 90°). Copper for example will wet zirconium and tantalum borides [16], vanadium carbide and chromium carbide [165] on heating up to 1200-1300°. Tin also forms a wetting angle of less than 90° at temperatures higher than 1200°C at the surfaces of WC (it should be noted that acute wetting angles with pure copper and tin were never observed for ionic compounds wetting where the compound had high strength ionic bonds: oxides of magnesium, beryllium, aluminium and covalent crystals boron nitride, diamond).

While interacting with, dissolving in or forming intermediate compounds with carbides, borides, nitrides and so on [182,183], the transition metals form non-equilibrium contact systems with the solid phase substance. This means that the value of W_a (non-equil) (the energy of the chemical boundary interaction accompanied by bond rupture in the solid phase) is added to the value of W_a (equil). The latter can be rather high for metallike phases at the interface with metals.

From the above general statements, one can assume that compound having high-strength interatomic bonds should interact with, and be wetted by, the liquid metal to a lesser degree. This

Reference

6°

Atmosphere

T°C

Metal

Compound

Table 18 (continued)

186	42	"	1100-1400	Cu	CrB_2	1500	42	186
186	39	"	1500	Ni	CrB_2	1500	39	186
186	55	"	1550	Co	CrB_2	1550	55	186
186	104	"	280	Sn	CrB_2	280	104	186
166	77-47	Argon	1100-1400	Cu	TaB_2	1300	118	166
166	43	"	1500	Ag	TaB_2	1500	43	166
166	50	Helium	1430	Cu	CrB_2	1480	50	166
166	11	"	1480	Ni	CrB_2	1480	11	166
154-28	8	"	1 min	Ni	MoB_2	1 min	8	154-28
148	148	Hydrogen	1100-1400	Sn	TiN	1500	148	148
155	135	Vacuum	1300	Cu	TiN	1300	135	155
186	53	"	900	Al	TiN	800	53	186
171	132	Ammonia	1550	Fe	ZrN	1130	132	171
171	146	Vacuum	1130	Cu	ZrN	1130	146	171
186	167	Ammonia	1500	Cu	ZrN	1500	167	186
186	140	Vacuum	900	Al	ZrN	900	140	186
186	49	Ammonia	1550	Fe	ZrN	1550	49	186
186	7	Vacuum	1590	Fe	ZrN	1590	7	186
171	150	Vacuum	1540	Co	ZrN	1540	150	171
186	130	Ammonia	1500	Cu	ZrN	1500	130	186
156	156	"	1130	Cu	ZrN	1130	156	156
171	150	Ammonia	1500	Cu	ZrN	1500	150	171
186	36	Vacuum	1130	Cu	ZrN	1130	36	186

statement is confirmed by the behavior of the metal borides [10,166]. Less stable diborides (MoB_2 , CrB_2) are better wetted by metals (copper, nickel) than more stable compounds (TiB_2 , ZrB_2 , VB_2).

According to the data from [178], a regular increase of the contact angle of wetting by liquid nickel, manganese, cobalt in the order TiC , ZrC , HfC is observed the greater the compounds stability.

Kemquist [165] has found that wettability of carbides by metals (nickel, cobalt, ferrum, copper) decreases with the increasing heat of formation of the carbide from its elements. The same observation has been made for a number of carbides (WC , NbC , VC , TiC) [174]. A decrease of the compound heat of formation can explain the data of reference [165] which shows a decreasing contact angle of wetting of titanium and tantalum carbides by liquid iron, cobalt and nickel on lowering the amount of carbon in the carbide below that of its stoichiometric content in the metal-carbide compound.

G. V. Samsonov [142,178] considered the intensity of the contact interaction and the degree of wettability from the atomic point of view through electron exchange to form stable electron states of atoms, which for transition d-metals are the states with d^0 , d^5 and d^{10} d-level structures [187]. In particular according to [178], the greater degree of wettability and the lower stability of the VIth group metal carbides to molten metals is attributed to the idea that the transitive metals of this group disturb the sp^3 electron states of carbon in the carbides favoring a greater percentage of nonlocalized electrons in the solid phase substance which can then bond with the liquid phase metals.

Carbides, borides and nitrides should be wetted by liquid metals to a different degree due to certain differences in the nature of the interatomic bonds in these compounds. Of the three types of compounds the carbides of the transitive metals [142] are characterized by a uniform distribution of electron density and by

the greatest metallic character of bonds and properties. Due to the presence of localized p-electrons there is a tendency to form covalent bonds between boron atoms (lattices and frameworks are formed by boron atoms) and perhaps between the atoms of boron and the metal. That is why these compounds are characterized by a reduced metallic character. In the nitrides of transitive metals, great asymmetry and non-uniformity of electron density distribution exist in the compound lattice. Thus the bonding should include a significant ionic component. This arises because of the higher ionization potential of nitrogen (14.47 eV) as compared to that of carbon (11.2 eV) and of boron (8.5 eV). This is why it can be expected that a higher value of the equilibrium part of the adhesion work - $W_a(\text{equil})$ is characteristic for metal carbides while a low value is more characteristic of borides and nitrides.

The thermodynamic stability of the compounds being considered increases from carbides to borides to nitrides. Evidently W_a will also decrease in the same order. Therefore one can suppose that wettability by liquid metals will decrease in the order carbide-boride-nitride. This is what is usually found experimentally (Table 19).

TABLE 19. A comparison of the wettability of metal carbides and borides by nickel at 1500°C [10] (The contact angles are given in degrees.)

TiC 0-10°	TiB_2 40°
ZrC 15-30°	ZrB_2 42°
TaC 16°	TaB_2 43-59°
Cr_3C_2 0° (positive coefficient of spreading)	CrB_2 11
Mo_2C 0°	MoB_2 8°

D. Wettability in the Solid Metal-Liquid Metal Melt System
Among the contact systems formed by metal melts, there are numerous examples which are of importance where the metal is the solid phase. Such combinations are used in various technological and physical processes, among which the following ones are of significance: (1) The manufacture of products by impregnating a solid skeleton with a liquid metal or by sintering in the presence of a liquid phase; (2) soldering, welding, and coating; (3) heat transfer in steam power plants and nuclear reactors [113,199,200]; (4) melt crystallization, modification, etc.; (5) the alteration of mechanical properties of solid metals under the influence of a liquid-metal medium [200-208]. In all of these processes, the phenomena occurring at the liquid metal-solid metallic interface, the value of the interfacial energy and the degree of wettability are of great importance.

Among numerous examples studied of contact between the liquid and the solid metallic phases [199,209-226,228-235] relatively few are devoted to quantitative measurement of wetting angles and interfacial energies [10,209,216,218,219,228-230,236]. The following methods of estimating the liquid metal wettability were applied in different works: (1) Visual observation of the liquid metal drop behavior at the solid surface and the establishment of the qualitative characteristics of the contact system ("spreading", "non-spreading") [232]; (2) determination of the spreading areas of standard weighed quantities of metal [210,217]; (3) determination of the possibility of obtaining stable films of liquid on the solid surface on immersing the latter in the melt or of the liquid complete running-off from it [210]; (4) direct measurement of the contact angle of the solid metal wetting by the liquid one; (5) measurement of the interfacial energy of the solid metal-liquid metal interface.

Works of this latter type are relatively few in number; measurements were carried out by the somewhat disputable method of dihedral angle or neutral drop [215,218,219,223,236]. In [222] the method of

zero creep is used and the interfacial energy of zincum coated by gallium is determined.

The most general observation concerning wetting in the systems under study is the relation between the wettability and the degree of bonding between the solid and the liquid metal, i.e. formation of chemical compounds, solid and liquid solutions and even the diffusion of the liquid metal into the solid one.

Hildebrand [193,212] has pointed to this relation. He notes that absence of wetting of the solid metal by the liquid metal is to be expected in cases when there are no chemical compounds formed, and no solubility between the metals.*

Just as formation of solutions is observed in metals with similar properties (in particular, specific bond energies, i.e. bond energy between atoms on a unit volume (c.c.) basis), non-wetting according to Hildebrand is to be observed in metals with sharply differing bond energies (if these metals do not form chemical compounds).

Tamman and Ruhenbach [211], Tamman and Arntz [213], Bailey and Watkins [210] underline the wetting angle dependence on the degree of diffusion of liquid into the solid metal. These scientists have carried out successive comparisons of wettability with the constitution diagram between the components of the contacting pair and interaction between them. Cases of non-wettability are found essentially in systems where there is neither interaction nor solubility [221].

The first studies of wettability in intermetallic systems were carried out using mercury. Tamman and Arntz [213], Alty and Clark [214] have visually observed the spreading of mercury over the surfaces of iron, copper, silver and tin. They have found that almost always a type of halo forms around the liquid drop which can be explained by surface diffusion of the liquid over the solid surface.

*The interrelation between the solubility of solid bodies in liquids and wettability in such systems is first mentioned in works by P. A. Rebinder [227].

Since the existence of the halo could be also attributed to evaporation and condensation of the liquid atoms, Alty and Clark have also investigated the rise of mercury along a tin capillary in an oil medium when there is no evaporation. In both cases a band of diffusible mercury atoms is formed over the front of the liquid.

Formation of a "matt spot" (halation) at the polished zinc surface near the edge of mercury drop (surface diffusion of mercury atoms) and difference between this process and the spreading proper of the compact layer of the liquid metal are shown in [202]. Regularities of spreading the halation front are generalized in [236].

Tamman and Ruhenback [211] describe their observations of liquid drops at solid surfaces for many systems within a substantial temperature range. The following systems have been studied: tin, lead, bismuth, silver - on iron; tin, lead, bismuth - on nickel; tungsten, molybdenum, tantalum, mercury - on copper, silver, gold.

According to the authors' definition, "non-wetting" means that, $\theta > 90^\circ$, "wetting" that $\theta < 90^\circ$. It has been found that mercury wets the surface of copper, gold and silver, forming a halo, at room temperature. At 350°C , tin, lead and bismuth do not wet the surface of iron. At $600\text{--}700^\circ\text{C}$ wetting by these metals (transition of the wetting angle through 90°) takes place in 30 minutes. In 60 minutes the drop has spread ever more forming a substantial halo.

Tin begins to wet nickel at temperatures about 400°C . Tin and lead behave similarly on nickel, but in the case of tin a great "crown" is formed in accordance with the fact that the solubility of tin in nickel is higher than that of lead.

In the Ni-Bi system when the temperature is increased up to 650°C , spreading is slowed down rather than accelerated. The authors attribute this phenomenon to decomposition of unstable compounds with temperature growth; at 470°C decomposition of the compound $\text{NiBi}_3 + \text{NiBi}$ can take place, at 640°C $\text{NiBi} + \text{Ni}_3\text{Bi}$.

A similar temperature effect on the wetting characteristics is observed in the system (tin-lead)-copper [210]. A stable coating of tin-lead alloy is formed at temperatures below 380°C (the tem-

perature of decomposition of Cu_6Sn_5 phase). This coating is destroyed as the temperature increases.

Usually a temperature increase facilitates wetting and the wettability increase is irreversible. In some cases spreading occurs on reaching a certain "critical" temperature.

The authors [211] have found that the wetting of molybdenum, tungsten and tantalum by lead and bismuth increases sharply on reaching a temperature equal to one third of the melting temperature of the solid phase. Perhaps this wetting is conditioned by an enhanced diffusion mobility of the solid phase atoms providing improved interaction in the contact zone.

The existence of a "wetting temperature" has been found for a eutectic solder of Sn-Pb on copper under a flux [56] as well as for the wetting of solid metals by liquid sodium [209].

A detailed study of the wetting of solid metals by liquid metals of spreading velocity and of coating formation has been carried out by Bailey and Watkinson [210]. Numerous data were obtained (though of qualitative nature) which relate the degree of wettability with the extent of interaction between the components of the system. During tests, the solid surface was coated with the liquid metal. After a certain time delay, the liquid metal was allowed to flow down the solid surface. The following states of the solid surface were observed (using the authors' terminology): (1) Wetting, formation of a thin continuous film of the liquid metal (in this case the wetting angle can be considered to be $\theta \approx 0$); (2) poor wetting, the liquid metal flowed down the surface but did not form a continuous film though adhering to the solid surface as individual drops (the wetting angle is finite but less than 90°); (3) non-wetting, the liquid does not adhere to the solid surface neither as a film nor as drops (evidently in this case $\theta > 90^\circ$).

These authors' data [210] about contact properties in these systems, organized in accordance with the observed degree of wetting are given below:

1. Stable coatings are formed in the system ($\theta = 0$):

Liquid - Solid	t°C	Chemical compounds are formed between metals		Liquid-Solid	t°C
Al - Fe	700	Zn	- Fe		500
Sb - Fe	700	Zn	- Ni		500
Sb - Ni	700	Zn	- Cu		500
Sb - Cu	600	Zn	- Au		450
Sb - Ag	550	Zn	- Ag		500
Fe - Fe	500	Pb	- Au		400
Fe - Ni	500	Bi	- Ni		400
Fe - Cu	400				
Fe - Ag	500				
Cd - Ni	400	Sn	- Fe		400
Cd - Cu	350	Sn	- Ni		400
Cd - Au	350	Sn	- Cu		400
Cd - Ag	400	Sn	- Ag		275

The solid metal is dissolved in the liquid metal

Ag	- Ni	1000	Pb	- Ni	400
Ag	- Cu	850	Pb	- Ag	300
Ag	- Au	1000	Bi	- Ag	300

2. No stable coatings are formed. Liquid metal adheres to the solid surface in the form of individual drops ($\theta \neq 0$, but less than 90°). This state is realized in the system:

Liquid - Solid		$t^{\circ}\text{C}$
Ag	- Fe	1000
Pb	- Cu	400
Bi	- Cu	400

3. Liquid metal flows completely off the solid metal ($\theta > 90^{\circ}$)

Liquid - Solid		$t^{\circ}\text{C}$
Pb	- Fe	400
Cd	- Fe	400
Bi	- Fe	400

It is seen that a high degree of wettability is observed in the presence of substantial interaction, the formation of a chemical compound or a solid solution; this is confirmed by the data of [226] where wetting angles are compared with a kind of phase diagram. When the phase diagram changes from the simple one corresponding to complete immiscibility of the liquid and solid states

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(systems Al-Pb, Fe-Bi, Al-Cd) to a more complex one with eutectics, solubility and chemical compounds (Zn-Pb, Zn-Bi, Zn-Cd, Zn-Fe, Sn-Cu, Al-Zn) the wetting angle decreases from 120-140 to 10-30°.

Bondi [56] has treated the data of a number of works determining the time of spreading of metal drops over solid metals and established the time needed to reach a given value of the wetting angle.

It has been stated that the time of spreading depends logarithmically on temperature and that the time decreases with increasing temperature. Hence it is possible to estimate the "activation energy" of the process. Values of this "activation energy of spreading" (V_A) for different systems are presented below:

System	$t^{\circ}\text{C}$	V_A , kcal/mole
Bi-Cu	400-700	5
Pb-Ni	400-450	29
Sn-Cu	300-350	31

Taking into account the uncertainty of the exact value of "activation energy of spreading," large errors of measurement, the use of different parameters by which the degree of wettability can be judged (in some cases the area of spreading, in other cases the wetting angle or the time of formation of a stable coating), the values obtained can be considered to be approximate. As to the order of magnitude (tens of kcal/mole) these values correspond to an activation energy of diffusion rather than to viscous flow of liquid metals.

On prolonged contact, the properties of the contacting phases and the degree of wettability can change. The following cases are possible:

(1) The solid phase tension can change due to adsorption of the liquid vapor. While being adsorbed on solid copper, lead can reduce the surface energy of copper from 1200-1300 to 700 erg/cm² [56]. At the moment of contact the energetic conditions are such that lead should spread over copper ($\theta \approx 0$), but adsorption is

taking place rapidly and soon the wetting angle becomes greater than zero (before the drop has time to spread completely), and finally the wetting angle of lead on copper reaches a value of between 40 and 60° (at $T = 400$ to 600°C).

At the same time, according to Lewis's data [217], lead under colohony or halloid flux at 350°C spreads rapidly over copper (the wetting angle value is not given). This is evidently attributed to the fact that lead cannot be adsorbed on copper through the flux and that the surface tension of copper remains high.*

(2) The degree of wetting is found to decrease with time following solid-liquid contact in systems forming chemical compounds. In this case a layer of an intermetalloid is formed at the interface which changes the interfacial energy. The final degree of wetting is determined by the relationship of the liquid metal properties and the intermetalloid being formed. As Milner states [220], the intermetalloid always resembles an ionic compound more than does the pure metal. Since ionic compounds are poorly wetted by metals, intermetalloid formation can adversely affect wetting. Examples of such systems are Ag-Sn, Ni-Sn, Fe-Sn [210] and Cu-Sn [210-218]. While immersing the solid metal in the liquid metal, the latter forms a coating on the former which reassembles into separate drops (de-wetting).

Studies of wetting on alloys has revealed the effect of intermetallic affinity and interaction. Thus lead being added to tin sharply increases the degree of wetting of steel and iron [221] (tin and iron form a stable intermetalloid); sodium at a concentration of 0.3% in lead decreases the interfacial surface energy at the boundary of liquid lead and zinc from 128 to 82 dyne/cm [224] (zinc and sodium also form an intermetalloid $Zn_{13}Na$); nickel added to lead (at a concentration of 0.1%) stabilizes the lead coating

*In general, if a σ_{SV} change takes place together with a substitution of the solid body then the σ_{SV} increase does not necessarily lead to an improvement in wetting.

on iron and copper [210] (nickel forms solid solutions with copper and iron).

Addition of indium to lead decreases the wetting angle of germanium [216]. Solubility of germanium in the liquid indium is higher than in lead; pure indium wets the solid surface of germanium more intensively than pure lead [216,225].

Prolov [221] has noted that wettability in the system metal-metal is the better the smaller the temperature difference of the fusion temperatures of the two metals, i.e. the more the metals resemble each other. This is confirmed by the data of Bailey, Fox and Watkins cited by Taylor [218] about interfacial energies and wetting angles of iron, nickel and copper for wetting by low melting metals (the data is obtained by the sessile drop and dihedral angle methods in vacuum):

Solid metal	Fe			Ni			Cu		
	Sn	Sn	Pb	Sn	Pb	Cd	Sn	Pb	Cd
Wetting angle, °	72	48	40	9	31	27	13		
Interface energy, erg/cm ²	640	470	540	280	200	100	140		

It can be assumed that differences in the properties of low melting elements and those of iron, nickel and copper, decrease from iron to copper (melting temperatures, electronic structure). The wetting angle and interfacial energy behave in the same way.

Large differences in the values of specific bond energies (heat of evaporation expressed on a unit volume basis and called by Hildebrandt the parameters of solubility) produce immiscibility or areas of stratification in liquid metal melts. Stratification occurs when

$$\frac{V_1 + V_2}{2} (\delta_1 - \delta_2) \geq 2RT \quad (24)$$

where $\delta = \frac{Q}{V}$, Q is the sublimation energy of the metal and V the atomic volume.

Thus when the properties of the contacting metals approach each other, there is a greater tendency for mutual solubility and diffusion, the interfacial energy is reduced, and the wettability of the system increases. With large differences between the properties of the components the opposite can occur; if metals differ in their specific volumes and energies but still have similar electrochemical properties then the wettability will decrease and interfacial energy will increase. In addition, when differences in their electronegativities increase there will be an increasing tendency to form intermetallics which, at least initially, will intensify the degree of wettability.

From the data cited above, the relation between the wettability in metallic systems and the intensity and character of intermetallic interaction, as well as the components properties in the contacting pair is clear. On another hand, studies [209, 220, 228, 229, 232, 235, 234] and experience in soldering and welding show that the adhesion properties of a liquid metal on a solid metal depend substantially on the presence of any oxide film. Such films are practically always present on contacting surfaces and hinder the true contact of metals. In [20] there is an example given which indicates considerable stability of such surface compounds. The oxide film at the surface proved to be stable at a temperature of 930°C and an oxygen pressure of about 1 atm, while the equilibrium constant for oxide dissociation is $1.7 \cdot 10^{11}$ atm at this temperature. In [10] the results are given of studying tungsten and molybdenum wettability by liquid tin, copper and silver, and the wettability of iron by lead. Some data are given in Figs. 30-32. Increasing the temperature decreases the contact angle sharply and irreversibly.

With continuous heating of molybdenum in contact with tin in vacuum or hydrogen and of iron with lead in hydrogen, the contact angle decreases and wetting occurs at temperature above 750 and 650° respectively. At temperatures below these "critical" values the contact angles are large (~120-130°).

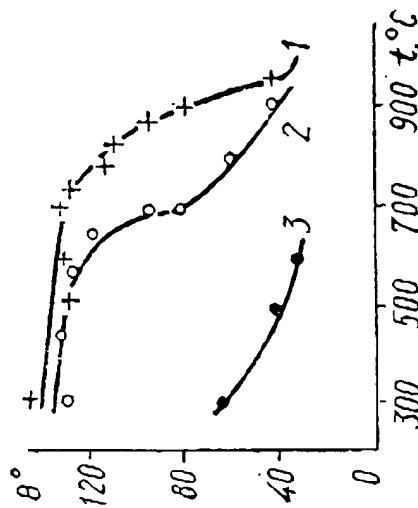


Fig. 30. Temperature dependence of the angle of contact of wetting of tungsten (1) and molybdenum (2) by liquid stannum; wettability in the system molybdenum-stannum after thermovacuum treatment of contact surfaces (3).

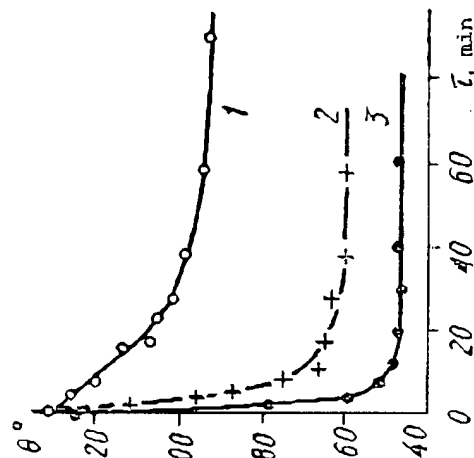


Fig. 31. Time dependence of molybdenum wettability by tin (vacuum): 1-700°C, 2-800°C, 3-850°C.

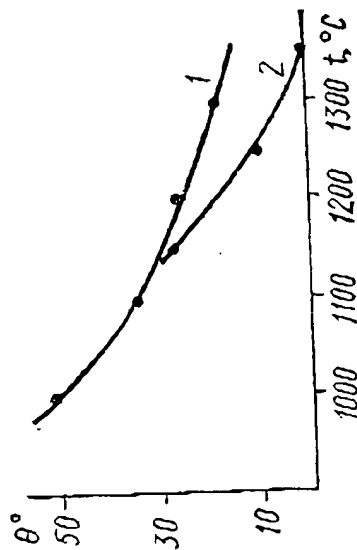


Fig. 32. Wettability of tungsten by liquid silver (1) and copper (2).

With a thermovacuum treatment of the surfaces of molybdenum, iron, tin and lead carried out by separately heating the solid and liquid metals to temperatures above the "critical" values, wetting can be achieved. The contact angle being 15-40° (at low temperatures (300-400°C) and high values of wetting angles were observed before thermovacuum treatment (Fig. 10, curve 3). Iron is wetted by lead at $T = 400^\circ\text{C}$ with a wetting angle of about 20° [10]. Evidently heating molybdenum and iron surfaces in a vacuum and a hydrogen atmosphere eliminates absorbed films from these metallic surfaces. These films are supposed to be oxides.

Molybdenum oxides are volatile in vacuum and are readily reduced by hydrogen. The oxide nature of these films is also shown by the following experiment with the system iron-lead. Short-term action of atmospheric air at room temperature on thermally clean iron surfaces reduces wetting and to reproduce wetting behavior, repeated thermal treating is needed.

Non-wetting in the systems tin-molybdenum and lead-iron, as well as abrupt changes of adhesion and wetting angle with temperature and time are, to a great extent, brought about by the presence of oxide films inhibiting direct contact of the liquid

and solid metal. Pure surfaces of molybdenum and iron are intensively wetted by tin and lead at the melting temperatures of the latter.

This conclusion can evidently be extended to other metallic systems, i.e. interaction between the solid and liquid metal in the contact layer, even for nonreacting systems, is sufficient to provide a high degree of wettability.

Both from the point of view of research methods and from comparison with the systems described above, the results of studying solid copper wetting by liquid aluminium are of great interest [239, 240]. The tests were carried out by placing molten aluminium onto the solid copper surface at the given temperature. A device with a "spoon" was used, the latter being made from beryllium oxide. The drop shape was recorded with the help of a camera.

Taking into account the tendency of aluminium to oxidize, appropriate measures were taken as to improve the experimental component purity. While the furnace was heating and initial equipment decontamination was proceeding, the vacuum in the system was still too low. During this time the spoon containing the aluminium (weighed quantity 0.6 g) was isolated from the furnace and remained cold. Only after the equipment was thoroughly heated and the high vacuum was at least $1 \cdot 2 \cdot 10^{-5}$ Torr was the spoon introduced into the furnace. It was possible in this way to obtain a pure shining aluminium surface which was very active in wetting solid bodies. If the spoon with aluminium had stayed in the furnace during the heating of the furnace and equipment decontamination, then even under high vacuum conditions (10^{-6} Torr) the aluminium surface would be covered with oxides and the tests would not have succeeded.

It should be noted that even ultrahigh vacuum conditions (10^{-10} - 10^{-11} Torr) though being favorable from the point of view of the experimental cleanliness, do not themselves lead to any substantial improvement of the contact surfaces (solid and liquid metal) in these studies. It is stated in [243] that liquid indium at $T = 160^\circ\text{C}$ forms an angle of contact of 170° at an aluminium surface

at a pressure of 10^{-10} Torr. This unusually high value of the angle of contact corresponds to the system In-Al₂O₃ and not to In-Al. The angle of contact of melted silver on niobium and tantalum was $> 90^\circ$ at 10^{-10} Torr [244].

In the system Al-Cu, due to special measures taken against contamination of the contacting surfaces and the active interaction of the solid and the liquid metal, good wetting was already observed at a temperature of 700°C and a vacuum of $1 \cdot 10^{-5}$ Torr. (It should be noted that in the system Al-Mo [245] the "wetting temperature" is more than 900°C . This is attributed to the less intensive interaction of aluminium and molybdenum).

Experimental data for the system Al-Cu are given in Fig. 33 [238]. Aluminium spreads over copper. Increasing the temperature accelerates the process but its influence is much weaker than for the systems lacking interaction between the components (Mo-Sn). Practically, the activation energy of the wetting process is estimated by measuring the time to achieve a certain value of the wetting angle (for the given system this value was chosen within the interval $30-50^\circ$) and plotting $\ln t \theta_0$ vs $\frac{1}{T}$ (see Fig. 34). This indicates that the activation energy for the system copper-aluminium (17 ± 4 kcal/mole) is much lower than that for the system Mo-Sn: 45 ± 5 kcal/mole.

While treating the phenomena of wetting in accordance with the above procedures, the contact systems solid metal-metallic liquid should be divided into two classes: (1) non-equilibrium systems where

$$\mu_i^s \neq \mu_i^l$$

(2) equilibrium systems where

$$\mu_i^s = \mu_i^l$$

Systems where the components are completely immiscible in the liquid and solid state below to type (2). For instance, pure iron (solid phase) is in equilibrium with pure lead (liquid). Diffusion,

dissolution of one metal in another, is absent in these systems as is any directed flow of particles from one metal to another.

Previously for such systems non-wettability of the solid metal by the liquid one ($\theta > 90^\circ$) was often found. But as experiments have shown [10], non-wettability in such systems is conditioned by the presence of contaminating films which hinder the true contact of the metals. With proper cleaning of the surface in such systems it is possible to obtain a high degree of wettability. This means that the contact of two metals due to metallic properties of the both is sufficient to slightly reduce the interfacial energy ($W_a(\text{equil})$ is close to cohesion work), i.e., the presence and influence of the field formed by the system of ions and electrons of a mobile metal and by the second metal charge density at the interface are such that they smooth sharp changes of electron density taking place at the metal-vacuum interface. In this respect, the theoretical computations of the surface interfacial energy with a simple (but perfect) metal contact taking no account of diffusion, dissolution and formation of intermetallics [241], i.e. of the equilibrium part of the interfacial energy are of great importance. Using these results one can estimate the wetting angle value in a system if it is assumed that one of the metals is liquid while the other is solid. To estimate the surface tension of the latter, Zhdankin's relation may be used:

$$\sigma_{sv} \approx 1.15 \sigma_{lv}.$$

Knowing this value and the value of interfacial tension from (241) it is possible to find the wetting angle from Young's equation. The results of such estimations for various pairs of metals are presented in Table 20. As is seen in most cases the interfacial tension values are so small that complete wetting (usually with a large positive coefficient of spreading) or at least wetting angles less than 90° will occur. Zero wetting angles with small positive or even negative values of the coefficient of spreading are typical of systems which incorporate metals with a low bond-

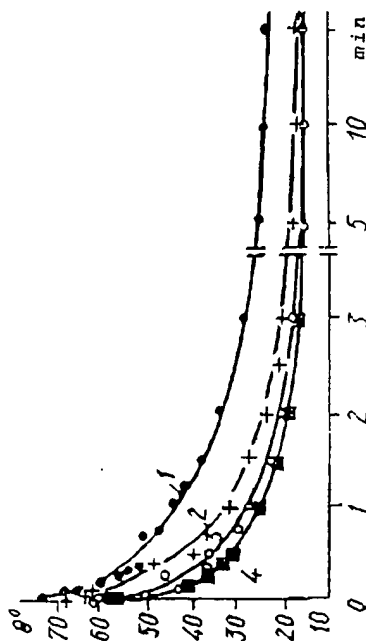


Fig. 33. Kinetics of liquid aluminium spreading over copper: 1-700°C, 2-800°C, 3-900°C, 4-1000°C.

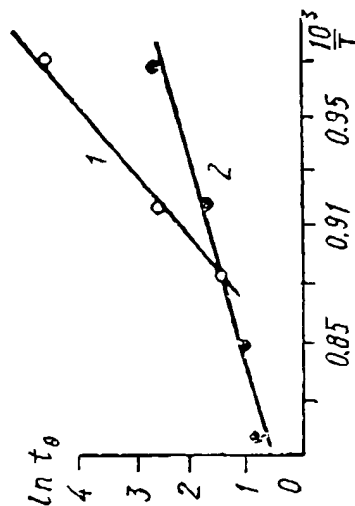


Fig. 34. Dependence of the period of "half-spreading" on temperature for systems tin-molybdenum (1) and aluminium-copper (2).

energy density (alkali metals like rubidium and cesium). Only few of the pairs formed by Ca, Sr and Ba have wetting angles close to 90° as can be observed where the solid phase metal tension is below that of the metal forming the liquid phase. It should be noted that the wetting angle values deter-

TABLE 20. Interfacial tension calculated theoretically [241] and estimated wetting angles in metal-metal systems.

Metal	σ_{Zn-Me} dyne/cm	θ_{Zn-Me} °	σ_{Cd-Me} dyne/cm	θ_{Cd-Me} °	σ_{Sn-Me} dyne/cm	θ_{Sn-Me} °
Zi	200/0		50/0		180/0	
Na	550/0		310/0		380/0	
K	710/0		360/0		630/60	
Rb	750/0		560/0		650/65	
Cs	790/0		600/0		730/90	
Cu	300/0		780/0		830/0	
Ag	25/0		180/0		270/0	
Au	20/0		250/0		390/0	
Al	150/0		350/0		360/0	
Ca	30/0		130/0		120/40	
In	20/0		0/0		20/0	
Be	300/0		520/0		520/0	
Mg	70/35		5/0		5/0	
Ca	140/70		50/55		60/50	
Sr	340/90		160/72		230/80	
Ba	370/90		20/85		260/90	
Zn	-		50/0		20/0	
Cd	50/0		-		350/50	
Hg	140/0		30/0		30/0	
Sn	20/0		0/0		-	
Pb	100/0		10/0		20/0	

mined by Young's equation as the difference of two approximately calculated values (σ_{sl} and σ_{sv}) depends strongly on errors of calculation and assumptions. Moreover it should be emphasized that in calculating interfacial tension [241] the authors did not take into account ionic, covalent or van der Waals component of the bond. Even under such conditions, zero wetting angle values are obtained in most cases. This confirms the conclusion that metal contacts form metallic bonds between the boundary layer atoms. This produces high values of W_a (equil) and a high degree of wettability.

The estimation of the interfacial energy in intermetallic systems carried out in [242] relative to the equilibrium part of the interfacial tension of equilibrium systems also predicts high wettability in the systems studied. At the same time, in systems

where a simple contact is the single cause of an interfacial energy decrease (i.e. in systems where there is no mutual diffusion or formation of intermetallics) the establishment of intermetallic bonds at the interface can be easily destroyed by the presence of contaminating films which inhibit perfect contact. An oxide film at the interface of these two metals increases the distance between the contacting surfaces and decreases the superimposition of electron orbits of boundary atoms while at the same time lowering drastically the intermetallic interaction. It is important that the system metal-film-metal remains stable since there is no tendency to movement and exchange of atoms between the phases: $\mu_i^s = \mu_i^l$. The solid metal is in thermodynamic equilibrium with the liquid one.

Quite another picture can be observed with the interactions of nonequilibrium systems. For such systems beside the purely contact process, interfacial energy can be decreased due to interfacial interaction (diffusion of one metal into another, formation of intermetallics at the interface or dissolution of the solid metal in the liquid metal, i.e. entrainment into interaction with deeper metal layers). Even in the presence of an oxide film between the contacting surfaces such a system is unstable. One or the both of metals tend to penetrate through the film as $\mu_i^s \neq \mu_i^l$. Such penetration, either spontaneous or initiated, was observed in published experiments [232]. If one of the pair of metals in the liquid state was placed on the oxidized surface of another metal and the film was not very thick then mutual penetration of atoms of both metals (or one of them) through the film can occur and further reaction (diffusion, dissolution) of metals may be observed.

The mechanism of penetration and formation of a good contact is as follows. According to [232] one of the metals, the liquid one, for example, reaches the solid metal surface (through the gas phase, for instance or through the faults in the oxide film). If the liquid metal dissolves the solid one, further reaction will take place preferably by dissolving the solid metal layers adjacent

to the oxide film (these layers are energetically rich, and dissolve quicker), i.e. the liquid spreads over the solid metal-oxide layer, interface separating the interlayer from the solid metal. Subsequently this process results in wetting and spreading of the liquid metal over the oxidized surface of the solid metal. If the film is too thick and the process of penetration does not proceed spontaneously it may be initiated by the local break of the oxide film under the liquid metal layer (for example by punching it with the needle). This creates a point contact between liquid and solid after which the process takes place spontaneously.

According to [209], a peculiar tunneltype mechanism of penetration through a faultless oxide layer of sufficiently small thickness is possible for the solid metal atom. Capillary flow of the liquid metal through cracks and pores of the oxide film, if the wettability of the oxide by the liquid metal is sufficiently high, simple dissolution of the oxide in one of the metals are also possible. Such mutual penetration of metals towards each other is accompanied by a decrease in the system energy and by a reduction of the difference between the chemical potentials of the components. These processes cannot take place in noninteracting equilibrium systems. Thus, in the system Cd-Al the system is as close to complete immiscibility of the components as possible according to calculations (see Table 20) and has a near zero value of the wetting angle. Unwettability of aluminum by liquid cadmium is found experimentally; the wetting angle is 145° [226]. This is attributed to the presence of an oxide film on the aluminum surface. Scratching the oxide layer at the interface, i.e. the creation of contact between the liquid and the solid metal initiates spread in the interacting system. Similar scratching proves useless for the system Cd-Al where spreading does not occur [232].

Rather large wetting angles in noninteracting systems (W-Sn, Mo-Sn, Fe-Pb) and their change with temperature and time are conditioned by the presence of intermediate oxide layers at the interface. These layers however are not always stable. Oxides of the

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corresponding solid metals are readily reduced in hydrogen and sublime at high temperatures, a factor which can explain a wettability increase with increasing temperature. A high "activation energy" of the wetting process (45 kcal/mole for Mo-Sn) is of the same order of magnitude as the dissociation energy of the corresponding oxide. $\Delta H_{298}^{\circ} = -60$ kcal/g-atom of O_2 and is evidently conditioned by the destruction of the oxide layers.

In the copper-aluminum system a partly reducible film is formed at the liquid metal surface. Due to mobility of the latter, one should expect numerous faults in the oxide film and good mutual penetration of metals through the film (especially if it is sufficiently thin; in a "poor" vacuum of 10^{-4} - 10^{-3} Torr, when the film becomes thicker, there is no wettability or spreading in this system). Thus, destruction of the oxide film is not the limiting stage of the process (evidently it is partially dispersed in the liquid metal and in the surface). Really the activation energy of the spreading process for the system under study is not high and is about 17±4 kcal/mole, a value which correlates well with the activation energy value of copper dissolution in liquid aluminium (16 kcal/mole) [237].

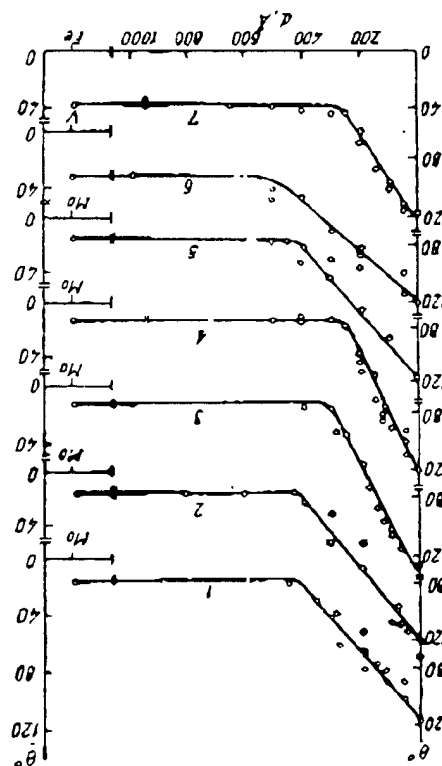
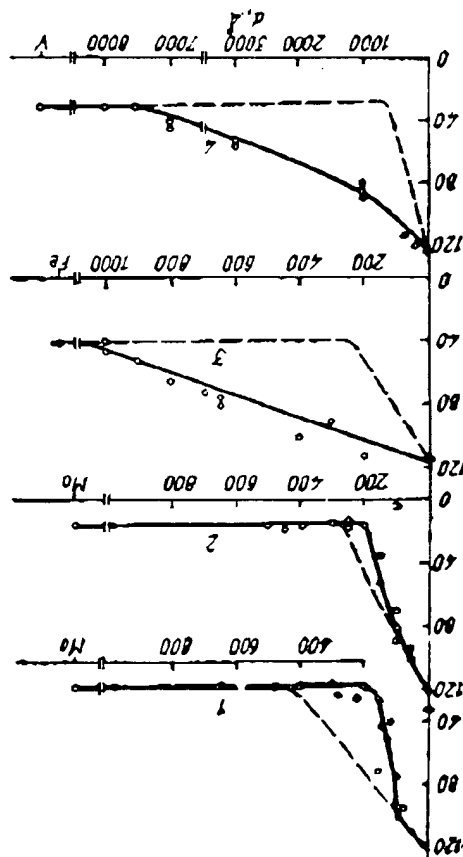
It may be assumed that the process of copper dissolution in liquid aluminium defines wetting and spreading in the system.

From the above discussion one can see the relation between the degree of wettability and the character and intensity of interaction between metals on one hand and oxide and other layers at the contact surface on the other. Both factors are acting jointly.

So the conclusion is that the metallic character of the contacting substances and a good intermetallic contact are, as a rule

Fig. 35. Wettability by metals of oxides (a) and graphite (b) depending on the metal coating thickness: (a) 1-Al₂O₃-Mo-Cu (1150°C); 2-SiO₂-Mo-Cu (1150°C); 3-Al₂O₃-Mo-Ag (1000°C); 4-SiO₂-Mo-Sn (900°C); 5-SiO₂-Mo-Sn (900°C)*; 6-SiO₂-V-Sn (900°C); 7-SiO₂-Fe-Pi (700°C); (b) 1-C-Mo-Cu (1150°C); 2-C-Mo-Sn (900°C); 3-C-Fe-Pi (700°C); 4-C-V-Sn (900°C).

*Preliminary annealing of the film at 1150°C (dotted lines present wetting in the systems similar to SiO₂)



sufficient to provide a low interfacial energy and a high wettability in the system. Cases of non-wettability in intermetallic systems are not observed on contact of pure surfaces. Nonwettability ($\theta > 90^\circ$) observed experimentally on contact of the liquid and a solid metal is due to the presence of intermediate oxide and other layers at the interface.

The Wettability of Metallized Surfaces of Solid Bodies

When it is necessary to increase wettability of solid metal bodies by metal melts, the former are subject to metallizing-coating with thin metal films. In such complex systems, wettability and adhesion depend on many factors (film thickness, the character and intensity of its interaction with the substrate and the liquid phase, etc.). Some questions of this kind are studied in [246, 247].

Studies have been made of the wettability of oxides (monocrystal Al_2O_3 -sapphire, quartz, glass) and graphite coated by evaporation of molybdenum, vanadium and iron films of different thickness and by melts of copper, silver, tin and lead. The dependency of the wetting angle on the coating thickness is shown in Fig. 35. The character of the dependence for most systems is the same; the wetting angle shows a neat linear drop from its value for the substrate pure surface to the value for the surface of the compact material film achieved at a certain coating thickness. The threshold value is different for various systems (from 150 Å to 7000 Å).

These results can be treated in the following way [246]. During the condensation of metals and film growth the film is not continuous while still thin, but has an insular or network structure. As the amount precipitated grows, depending on the annealing temperature; the islands are also growing (at the expense of coagulation) and the film becomes continuous only at a certain critical thickness, which depends on several factors, in particular on adhesion of the deposited metal to the substrate. Thus metallic conden-

sates in the form of continuous films on metallic substrates can be obtained at much smaller total film thickness than on nonmetallic substrates. These substrates are "unwetted" by solid crystallites or condensate nuclei, and their relative area of contact with the substrate is smaller.

For heterogeneous surface in contact with the liquid phase, the total adhesion work can be put down as follows:

$$W_a = W_{a1} \cdot S_1 + W_{a2} \cdot S_2 \dots \quad (25)$$

where W_{a1} and W_{a2} are specific adhesion works of the melted metal on different sections of the solid phase surface (either pure or coated by deposited metal), S_1 and S_2 are, respectively, the portion of the substrate surface still uncoated and that covered with condensate ($S_1 + S_2 = 1$).

S_2 growth alone will cause an increase of the degree of wettability of the substrate by the liquid metal as the film thickness on the substrate increases. The critical thickness is smaller at a lower annealing temperature, with greater adhesion of the film to the substrate and good wettability of the substance reaction products with the substrate. From Fig. 35a it follows that for a molybdenum film the critical thickness on oxides SiO_2 and Al_2O_3 with wetting by copper is 250-450 Å, depending on the film annealing temperature. For graphite coated by molybdenum (Fig. 37b) this thickness is smaller and is about 150 Å (there is a high adhesive interaction between Mo and graphite). Because of the poorer wettability of vanadium carbides and iron by metals as compared to pure vanadium and iron, the critical thickness of films in the graphite-vanadium system and the graphite-iron system (liquid metallic phase tin and lead) shifts to about 10^3 Å.

An improved formula for the wetting angle of a solid body surface coated by an insular structure film, taking into account the contribution of the nuclear form of the film to its adhesion to the substrate is given in [246].

V. CONCLUSION

The study of adhesion and wettability of solid bodies by metal melts has recently made substantial progress. A number of adequately improved methods of measurement have been developed. A great amount of experimental data on wettability in a wide variety of systems is now available. A general analysis of the data obtained has permitted the derivation of theoretical statements which have allowed us to understand and explain some common features of the process.

A chemical interpretation of the phenomenon of solid body wettability by liquid metals and an interpretation of the process as a chemical reaction in the interphase area makes it possible to calculate quantitative values of the strength of adhesion and of the wetting angle value in specific systems.

Recently some studies have been devoted to elucidating the connection between the degree of wettability, the character and type of interphase interaction (dissolution, diffusion or chemical compound formation) and the nature and properties of newly-formed interface layers.

The technique of measuring interfacial energies at the boundaries of solid phases is being improved though these data are not yet in complete agreement with the values of interfacial energies obtained from the wetting angle equation.

The results of these basic studies of the wettability of solid bodies by metals are used now to solve many technical problems.

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